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Environmental Application of Nanoparticles Copper Oxide

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DEDICATION

To all knowledge and science seekers,

To everyone who lightened a candle on the road of knowledge for others,

To everyone who dedicate his life to learn and teach other,

To all of these people, hoping that I am among them, I dedicate this humble work.

Acknowledgement

This study is result of dedicated effort of many individuals, several of whom deserve special mention: I thank Joseph Hill, Dean of the Faculty of Science, UAE University, for offering me the chance to join the Environmental Science Master Program, I greatly appreciate my supervisors Dr. Abbas Khalil and Dr. Saeed Bukallah from the Chemistry Department, Faculty of Science, UAE University, for their suggestions, continuous guidance, supervision and patience through out the study, and their efforts in the completion of this study. I thank my colleagues in the Chemistry labs, Faculty of Science, UAE University for their valuable cooperation.

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ABSTRACT

The work presented in this thesis involves a series of studies carried out towards the two main goals of this project. The first goal is to prepare high-surface-area pure copper(II) oxide and composites containing copper(II) oxide. The second goal is to investigate the catalytic reactivity of these materials toward the adsorption and decomposition of the environmentally hazardous chlorinated hydrocarbon compounds (CHC).

The first part of this work involves several studies to prepare ultra fine powder of pure copper oxide. Forced precipitation method has been employed starting with copper(II) chloride or copper(II) nitrate nonahydrate as the precursor. Besides varying the precursor, a variety of solvents have been investigated. Promising results have been obtained where high-surface-area powders of CuO have been obtained using ethanol or t-butanol as the solvent. TGA, FTIR, and powder x-ray diffraction studies have shown that the initial $Cu(OH)_2$ product converted completely to CuO at temperatures between 180 and 250 °C. The surface area of the CuO depends on the calcinations temperature where specific surface areas in the range of 40-60 m^2/g were obtained after calcination at 250 °C. Besides the pure CuO, composites containing CuO supported on activated carbon, Al_2O_3 and TiO_2 have been prepared, through wet impregnation method, and characterized.

The second part of this work involved several reactivity studies to investigate the capability of these materials to adsorb and catalytically decompose C_2Cl_4

and CCl_4 as representative CHC compounds. Significant results have been obtained in this direction that resulted in a series of important conclusions. One of the most significant conclusions established was the remarkable catalytic reactivity that TiO_2-CuO exhibited towards the decomposition of C_2Cl_4 in the presence of water producing CO_2 and HCl without the formation of any of the undesired products $COCl_2$, CO, and Cl_2. C_2Cl_4 is known for its stability toward the adsorption and decomposition on metal oxide surfaces which makes such results very interesting and promising towards the optimization of practical catalytic systems for these environmentally important processes.

List of Contents

List of Tables

Chapter One

Chapter Two

Chapter Three

List of Figures

Chapter One

Chapter Two

Chapter Three

CHAPTER 1

INTRODUCTION AND BACKGROUND

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1.1 Heterogeneous Catalysis

A catalyst is conventionally defined as a material that facilitates chemical reactions but itself is not consumed in the course of the reaction. Heterogeneous catalysis, refers to the process where the catalyst and the reacting materials exist in different physical phases. Usually the heterogeneous catalyst is a solid, crystalline or amorphous. Catalysis by solid materials has been observed quantitatively at temperatures as low as 77 K and as high as 1500 K. Reactants are usually in the gas phase or in polar or nonpolar solvents; with or without assistances of radiation, or electron transfer at electrodes. Catalysts can be pure metals as unreactive as gold and as reactive as sodium or multicomponent and multiphase inorganic compounds as well as organic polymers [1].

With these facts in mind, the task of presenting the principles of heterogeneous catalysis is a daunting one. Indeed, the chemistry of catalysis is as varied as chemistry itself. Moreover, the related subjects cover many disciplines: surface science; inorganic, organic and organometallic chemistry; physical chemistry and spectroscopy; theoretical chemistry; metrials science; modeling and molecular graphics; and catalytic reaction engineering. There exist catalytic materials that are interesting but not applied. Then there are model catalysts that serve as standards for comparison with catalytic materials and commercial catalysts. Only the latter are robust, economical and complex, but their physical

and chemical characteristics depend frequently on several, variables.

Principles of heterogeneous catalysis are more likely to be formulated following the study of model catalysts in ideal reactors than from performance data obtained with commercial catalysts. The latter are obtained with impure or mixed feedstreams reacting in complex reactors made of practical materials.

1.2 The Catalyst and the Catalytic Cycle

The classical definition of catalyst has been discussed many times. In one definition, a catalyst is a substance that changes the kinetics but not the thermodynamics of a chemical reaction. In another definition, a catalyst is a substance that transforms reactants into products, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated in its original form at the end of each cycle during the life of the catalyst [2].

The catalytic cycle is the principle of the catalytic action. The activity of the catalyst is defined by the number of revolutions of the cycle per unit time, or turnover rate or turnover frequency (TOF). The life of the catalyst is defined by the number of turnovers observed before the catalyst dies. This number must be larger than unity; otherwise the substance used is not a catalyst but reagent. Catalyst life can be very short, as in catalytic cracking of oil, or very long, corresponding to as many 109 turnovers in ammonia synthesis [1]. In heterogeneous catalysis, the catalytic substance is found as an active site or active center at the surface of a solid. Inorganic solid catalysts include a variety of materials including carbon, metal particles, metal oxides, metal

sulfides, metal nitrides, and organometallic compounds. These solids need to be activated, for example reduced, before they work as catalysts. For true catalysis, the complete cycle must be carried out without interruption in a single reactor. Catalytic reactions are still discovered and developed long before their mechanisms are understood at even a qualitative level.

1.3 Surface Structures

Structures of solid surfaces are notoriously complex and difficult to elucidate. Surfaces of most catalytic solids have microscopic regions with different compositions, phases, and structures, each with variety of imperfections. The structures are difficult to determine under the best of conditions (e.g., in ultra-high vacuum) and are often almost impossible to determine under the conditions of a catalytic reaction. Because surface catalysis rests on such a weak structural foundation, it is only poorly understood in comparison with solution catalysis, and the best available models of most catalytic sites and reaction intermediates are vague and tentative. The simplest solid surfaces are those of single crystals, especially of metals being made of only one kind of atom. The surface structure depends on both the bulk structure and on the manner in which the bulk is terminated; it can be cleaved to expose various planes having different configurations of atoms. The surfaces with steps and kinks, such as those shown in Figure 1.1, more nearly resemble the structures of typical catalyst surfaces (with their nonuniformities) than do the simpler structures [3].

These single-crystal surfaces are ideal models of more typical surfaces. The step and kink structures illustrate how surfaces are nonuniform (heterogeneous) on an atomic scale. There are also other kinds of nonuniformities (or defects) in surfaces. Point defects are either adsorbed atoms or vacancies (where single atoms are missing from the lattice). Surface defects on a larger scale almost always exist, and some can be detected by microscopy. There may be dislocations in a crystal due to a mismatch of atomic planes; these show up as line defects. Dislocation densities of the order of 106 to 108 per square centimeter are typical of metal or ionic single-crystal surfaces, and densities of 104 to 106 per square centimeter are typical of metal oxides [3].

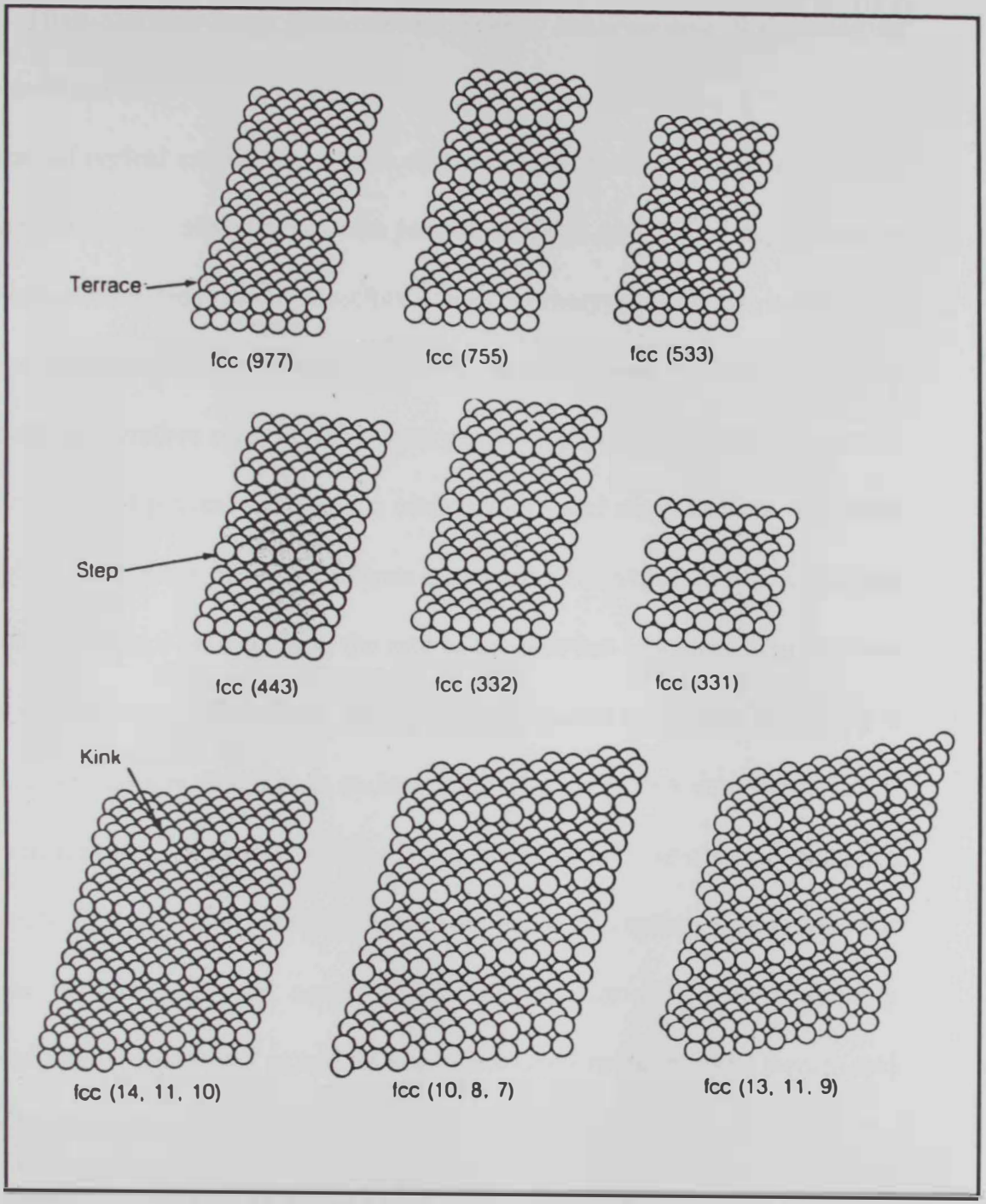

Figure1.1 Structure of stepped surface of a face-centered cubic (fcc) metal showing step and kink sites [4].

1.3.1 High-Surface-Area Amorphous Solids, Macroscopic Structures of Porous Solids

Surfaces of typical catalysts are quite different from those of single crystals. A catalyst particle usually consists of a jumble of small crystallites aggregated in to a high-surface-area porous structure. These primary particles are usually too small to yield to structural determination by X-ray powder diffraction, and the bulk solid is therefore referred to as amorphous. The small crystallites expose a variety of crystal planes with various compositions and many defects. The need for high surface areas of solid catalysts is easy to understand: When a catalytic reaction takes place on a surface, the rate of the reaction increases in proportion to the surface area. Therefore, the optimum form of a catalyst is usually a porous solid that has a high as is surface area. The only other way to produce a high surface area per unit volume of reactor is to use minute particles (extremely fine powders). Practical concerns make this option unrealistic. For example, the pressure drop across a fixed-bed reactor would be intolerably high, and the fine particles would be easily entrained in the product stream and plug downstream pumps and lines.

1.3.2 Surface structures of metal oxide

Most catalytic materials are amorphous and cannot even be prepared as single crystals that would allow exact determinations of surface structure. Many metals and few metal oxides (e.g., TiO_2 and MgO) have been prepared as single crystals and have been investigated with ultra high vacuum techniques [3].

The best available characterizations of most catalytic materials are based on inferences from the bulk structure (which by themselves can often be misleading), combined with evidence of surface composition and identification of functional groups determined spectroscopically (e.g., -OH groups on metal oxide surfaces). The most valuable characterizations of surface functional groups are obtained with organic adsorbates as probe molecules [5]. Examples of important metal oxide systems that exhibit different surface properties include MgO and Al_2O_3 which will be discussed in some details next.

Examples of important metal oxides systems that exhibit different surface properties include MgO (3,6) and Al_2O_3 (7). Al_2O_3 will be discussed next in some details.

1.3.2.1 γ-Al_2O_3

γ-alumina is the most widely applied catalyst support and has been used itself as an active catalyst. γ-Al_2O_3, one of the family of transition aluminas, is usually made by heating $Al(OH)_3$ at temperatures between 500 and 900°C. As the solid is heated in air, it is decomposed into an oxide with a micropore system and a surface area of hundreds of square meters per gram. Raising the temperature to about 1100 C leads to further transformation of the solid, with changes in structure of the primary particles and collapse of the pore structure, leading to loss of almost all of the internal surface area and ultimately giving the stable and extremely hard crystalline α-Al_2O_3 (corundum, made up of linked AlO_6 octahedra) [7].

Transition aluminas are the most widely used support materials for catalysts for several reasons. They are inexpensive, stable at relatively high temperatures (even under hydrothermal conditions, i.e., in the presence of steam) mechanically stable, easily formed in processes such as extrusion into various shapes (typically, cylinders) having good physical strength, and easily formed with a variety of pore structures [3].

γ-Al_2O_3 is an amorphous solid having a defect spinel structure (spinel is the mineral $MgAl_2O_4$) with layers of O^{2-} ions in a cubic close packed arrangement and layers of Al^{3+} ions, some having tetrahedral and some having octahedral coordination in the oxygen lattice. The bonding is intermediate between the ionic bonding of MgO and the covalent bonding of SiO_2 [3].

Heating the fully hydroxylated γ–Al_2O_3 under vacuum to temperatures exceeding 200°C leads to dehydroxylation, as depicted schematically in(Fig.1.2) [5]. The degree of dehydroxylation of the surface can be regulated by heat treatment temperature [8]. This process leads to the formation of coordinatively unsaturated O^{-2} ions and adjacent surface anion vacancies. It also leads to the exposure of coordinatively unsaturated Al^{3+} ions. Therefore, the dehydroxylation creates Lewis acidic as well as Lewis basic sites on the surface [3].

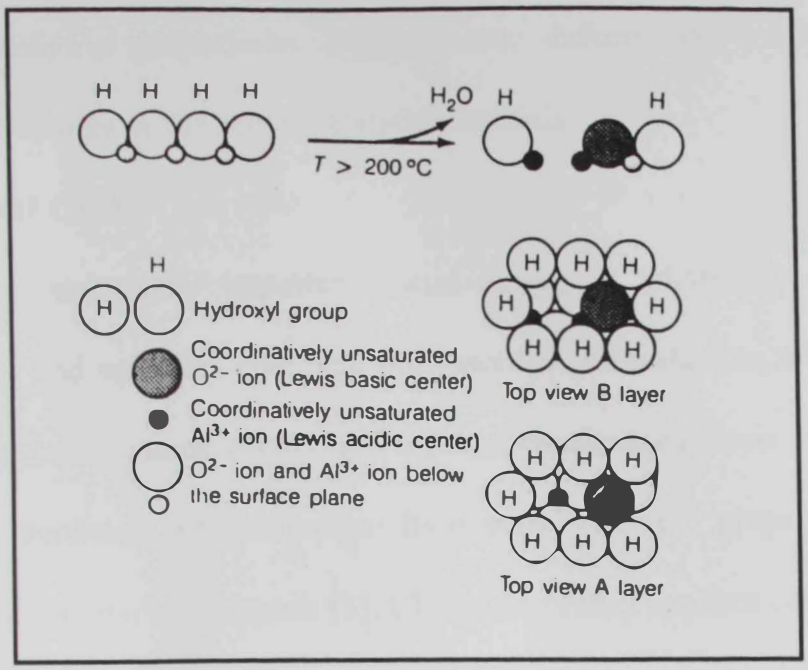

Figure 1.2 Simplified representation of the dehydroxylation of the (111) surface of γ-Al_2O_3 showing two structures of the resulting Lewis acid-base sites.

The acid-base properties of the surface have been investigated by titration and by adsorption of organic probe molecules and measurement of their infrared and NMR spectra. The surface -OH groups act as Bronsted acid sites and can act as basic sites. Bifunctional adsorbates such as alcohols, with proton donor and proton acceptor sites, interact with the acid-base pair sites on metal oxide surfaces.

The structural models usually show particular crystal faces, but metal oxides used in the form of an amorphous material expose a variety of crystal faces in

various and unknown proportions. Furthermore, defects and impurities complicate the structures of the actual catalytic materials.

1.3.3 Mixed Metal Oxides

There are many catalytically important metal oxides in addition to those mentioned above, and some are combinations, such as silica-alumina mixtures which have been used extensively as hydrocarbon cracking catalysis prior to the advent of zeolites. Silica-alumina hydrogens can be prepared by coprecipitation of the two components [3]. Charge neutrality requires cations at the surface, and silica-alumina has both Lewis and Brönsted acid sites, some of the latter being very strong.

Some other mixed metal oxides are also strong acids; some are even superacids. The acidity can be enhanced by adsorption of Lewis acids like SbF_5 on solid Brönsted acids, such as silica-alumina; others are formed by sulfating solids such as zirconia.

1.4 Surfaces and Catalysis

1.4.1 Catalysis on Functionalized Surfaces: Connections to Molecular Catalysis

When a catalyst consists of functional groups such as acids, bases, and metal complexes grafted to a nearly inert support, then the catalysis may be very similar to that occurring in a solution of analogous functional groups, and the catalytic sites are easily identified as the functional groups. The silica-supported metal complex groups, for example, provide some of the most direct connections between solution catalysis and surface catalysis [3].

There is a variety of industrially important processes that depend on such catalysis. One example is silica-supported Rh complexes that are used for forolefin hydrogenation and hydroformylation, among other reactions [3]. What is important about these supported metal complex catalysts is the conceptual bridge they form, linking solution and surface catalysis; the chemistry is in essence the same whether the catalytic group is dissolved or supported.

1.4.2 Catalysis on Metal Surfaces

Some metal catalysts are used in the form of powders or screens (gauzes) in industrial processes, but most are used in the form of highly dispersed aggregates on supports. One reason why highly dispersed metals are preferred is that many of the industrial catalytic metals are very expensive, and it is efficient to have most of the metal exposed at a surface and accessible to reactants. Typical supports are robust porous solids, including metal oxides, such as alumina and silica, and carbon. One of the famous supports is high-surface-area silica, SiO_2. The surface is that of the aggregated primary particles, which are noncrystalline (hence the term silica gel). In comparison with surfaces of most metal oxides, the silica surface is nearly inert. The most reactive groups are the -OH groups (called silanol groups) that terminate the primary particles; these are weakly acidic, comparable to alcohols. The bulk may be terminated entirely by -OH groups, which can be removed by dehydroxylation [3].

Molecules are activated by metal atoms on metal surfaces much in the way that they are activated by metal atoms in metal complexes. For a reactant to be activated, it must be bonded to the metal, which requires coordinative unsaturation. Metal surfaces offer a marked advantage over metal complexes in this respect; they can be made to be coordinatively unsaturated (e.g., by treatment under vacuum to remove adsorbates) without loss of their structures. Metal complexes and clusters, on the other hand, are usually unstable when they have even low degrees of coordinative unsaturation. Many metals have catalytic activity for many reactions. In practice, the catalytically important metals include most of the transition metals that are important in metal complex catalysis; the platinum group metals find especially wide use, even though they are expensive [3].

Metal surfaces offer many opportunities for catalysis that are not offered by metal complexes. Because the metals are robust, they can be used efficiently at temperatures that are too high to be practical for solutions and too high for the stability of most metal complexes in solution or anchored to supports. One of the important processes that depend on metal catalysts is hydrogenation of organic compounds.

Another important reaction that takes place on surfaces of metals is the CO oxidation which is catalyzed by platinum group metals .

$$CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 \qquad (1.1)$$

This is environmentally and technologically important, as it occurs in tens of millions of catalytic reactors in automobiles, helping to reduce the air pollution

resulting from exhaust. These metals catalyze a number of reactions in addition to the oxidation of CO, also converting unburned hydrocarbons and nitrogen oxides [9]. A deep understanding of the surface catalysis has evolved from characterization of the adsorption of CO and oxygen combined with a series of kinetics measurements [3].

1.4.3 Catalysis by Metal Oxide Surfaces

Research on single crystals of metal oxides has developed much less rapidly as compared with metals. This is, in part, due to the fact that metal oxides are poor electrical conductors and build up charge when bombarded with electrons, which hinders ultrahigh-vacuum electron spectroscopy experiments [3].

Metal oxides exhibit wide range of acid and base characteristics. The proton donor groups are usually -OH groups, and the Lewis acid sites are exposed metal ions. The basic groups are usually oxygen ions and -OH groups. As in solution acid-base catalysis, the important elementary steps on the surface involve transfer of protons and hydride ions, and the catalytic activity may be simply related to the proton donor strength, although sometimes the chemistry is more subtle involving the concerted action of proton donor and proton acceptor groups [3]. A good example that illustrates these ideas is alcohol dehydrations which are among the most thoroughly investigated reactions catalyzed by metal oxides [10].

1.4.4 Catalysis by Mixed Metal Oxide:

Mixed metal oxides, those containing more than one kind of metal atom in the bulk, are important catalysts that are used widely in several processes

including selective oxidation of hydrocarbons. The surface of a mixed metal oxide exposes two different metal ions in addition to O^{2-} ions and -OH groups. Selective oxidation of the hydrocarbon, represented schematically in (Fig 1.3), usually occurs at surface sites having oxygen atoms of limited reactivity (associated with metal M_1 in the figure), and these react with the hydrocarbon to give water and a partially oxidized organic compound rather than the undesired CO_2. These surface sites are then reoxidized indirectly and not by O_2 from the gas phase. The O_2 reacts instead with a surface site associated with the second kind of metal ion (M_2), and oxygen is transported as ions through the bulk of the catalyst from the second site to the first to reoxidize it, with a compensating transport of electrons to complete the cycle [3].

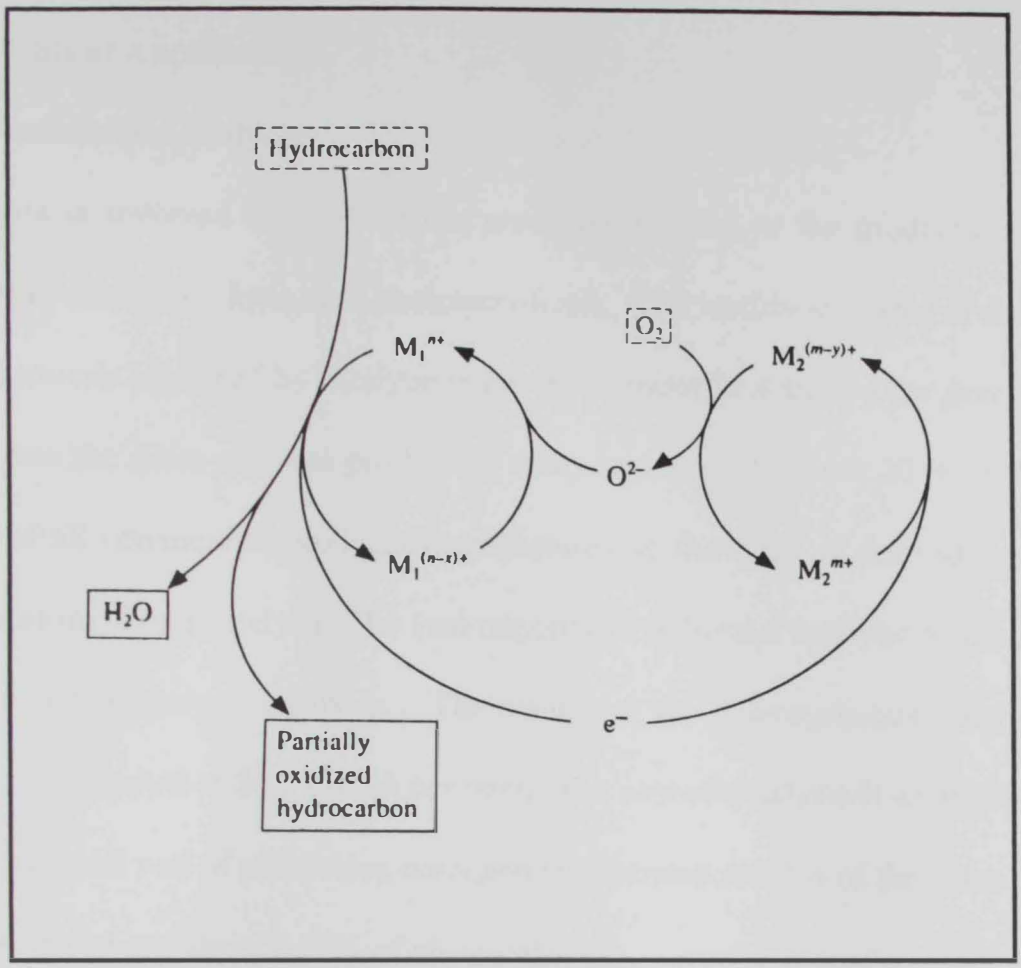

Figure 1.3 Schematic representation of the catalytic cycle for ammoxidation of propylene and related surface-catalyzed partial oxidations. M1and M2 represent the two metals in the mixed metal oxide catalyst.

1.5 Fields of Application

1.5.1 Industrial Catalysis

Catalysis is involved in most of the processes leading to the production of industrial chemicals, fuels, and pharmaceuticals. The worldwide value of fuels and chemicals produced by catalytic reactions is about $2.4 trillion per year, or more than the gross national product of many nations [1]. About 20 % of the value of all commercial products manufactured in the USA is derived from processes involving catalysis. The vast majority of industrial catalytic reactions involve heterogeneous catalysis. The value of the heterogeneous catalyst market is estimated at $6.5 billion per year. The cost of catalysts is normally a relatively small part of processing costs and is estimated at 0.1% of the value of fuels produced and about 0.22% of chemicals [1].

Industrial catalysis has developed slowly from an art to a science and, even today, many industrial processes are based on enlightened empiricism more than on derivation from scientific knowledge. Whereas other relatively small-scale uses of catalytic reactions occurred in the 19th century, the first major breakthrough of modern industrial catalysis was the fixation of nitrogen by the Haber-Bosch process [11] which was commercialized in 1913. From about 1910 on, industrial catalysis rapidly gained importance until it dominated chemical processing by the middle of the 20th century. Its growth was stimulated considerably by the industrial needs of two World Wars, and by the discovery of vast resources of petroleum, which changed the energy balance of

the world trade [12]. Examples of important processes related to petroleum industry include hydrocarbon cracking and oxidation of hydrocarbons.

Another example is the conversion of methanol to gasoline (MTG). In 1982, the methanol to gasoline process was commercialized in New Zealand with the construction of a 750000 ton per annum plant to convert natural gas to gasoline via methanol. The process uses the shape-selective properties of ZSM-5. The shape selectivity of zeolites was discovered in the mid-1960s and has since found many applications. Its importance continues to grow. It is based on the concept that the pores of certain zeolites in which chemical reactions are catalyzed are of the same order of size as the molecular dimensions of the reacting molecules. Depending on the size and shape of reacting molecules, they may or may not diffuse into the zeolite, and some potential reaction products can, for steric reasons, not form in the zeolite pores. The concept of shape selectivity is finding increasing applications in the synthesis of polymers and of pharmaceutical, agricultural, and enzymatic syntheses [1].

1.5.2 Environmental Catalysis

Besides their wide use in industrial applications, adsorbents and heterogeneous catalysts has shown a variety of potential applications in the field of environmental clean up and pollution control. Increased consciousness by the public of the health hazards of many toxic materials emitted into air and in water during chemical manufacturing and other processes such as disposal of nonbiodegradable products, has led to a rapid increase in efforts to ameliorate

toxic effects and environmental damage. Most of the processes developed thus far involve catalysis.

The first impact of environmental concerns [13] occurred in the early 1960s with the recognition that automobile emissions caused a serious health hazard as did the use of tetraethyl lead as a gasoline additive. There had been significant scientific research on the conversion of carbon monoxide and of nitrogen oxides. Various automobile and petroleum companies have invested in great deal of research to come up with a catalytic technology to meet the required standards for CO and NOx emission from automobiles. The success of this effort is shown in Table1.1.

Table 1.1 Average emissions from gasoline cars as grams per mile over Environmental Protection Agency (EPA) fedral test procedure [14].

			Hydrocarbons		
Year of model	CO	NO_x	Exhaust	Evaporative	Total
Zero miles					
1966	78	3.4	7.2	4.5	11.7
1986	1	0.5	0.2	0.6	0.8
Reduction (%)	98	84	97	88	93
50000 miles					
1966	89	3.4	8.1	4.5	12.6
1986	13	1.3	1.0	0.6	1.6
Reduction (%)	85	62	88	87	87

Automobiles exhaust gases from spark-ignition automobiles contain harmful CO, NO_x and hydrocarbons (incompletely combusted fuel constituents). Automotive converters using oxidation catalysts which were introduced in the US in 1975, convert CO and unreacted hydrocarbons to CO_2 and H_2O. Three-way automotive converters catalyze these oxidation reactions and also simultaneously reduce nitrogen oxides [1].

Modern three-way converter catalysts control CO and hydrocarbons by oxidation. Simultaneously, NO_x is removed by reduction, according to:

$$2CO + 2NO \longrightarrow 2CO_2 + N_2 \qquad (1.2)$$

$$HC + 2NO \longrightarrow CO_2 + \tfrac{1}{2}H_2 + N_2 \qquad (1.3)$$

The generic converter catalyst was invented in the early 1950s. Catalytic materials in automobile converters are generally supported on a ceramic honeycomb monolith made of cordierite ($2MgO\ .2Al_2O_3\ .5SiO_2$) containing 30-60 square channels per square centimeter. The honeycomb is coated with a layer of activated alumina called the washcoat. Catalytic Pt, Pd, and Rh are highly dispersed on the high-area washcoat. Rhodium metal displays high activity for the removal of CO, HC_s, and NO_x, and is particularly important for the reduction of NO_x. Fresh Pd is more active than Pt in most cases for CO, NO_x, and hydrocarbon conversion, but is more susceptible to poisons such as lead and sulfur, and sinters rather easily in a reducing atmosphere[1]. Ceria may be added at a loading of 2- 30 wt % to the washcoat of three-way catalysts to store oxygen, to promote the water-gas shift reaction and to stabilize the noble metals against thermal damage. Nickel can be added to scavenge H_2S [1].

Although it is estimated that 96% of the exhaust HC and CO and 76% of the NO_x can be eliminated by the use of catalytic converters, there are needs and opportunities for improvements [1].

Some other examples of environmental catalytic processes include removal of phosgene during the production of methylenediphenyldiisocyanate, removal of H_2S from gas streams, decomposition of CHC, and removal of a wide range of other volatile organic compounds (VOC). In all these cases, catalysis has been found or is being investigated to play major role.

The contribution of catalysis to the decrease in air pollution as an example has been reported for the period 1966-1986 showing a 90% reduction in carbon monoxide emissions, 30% reduction in SO_2 emissions, and 70% reduction in NO_x emissions [1]. With these great achievements, there are still needs and opportunities for improvements. Since the subject of this thesis deals with copper oxides and chlorinated hydrocarbons, in the rest of this chapter we will focus on chlorinated hydrocarbons and their environmental impacts then the role of copper oxides in environmental catalysis will be discussed.

1.6 Chlorinated Hydrocarbon Compounds (CHC)

Chlorinated organic compounds are among the most resistant pollutants for removal by sorption or catalytic destruction. Several literature reports have demonstrated that some reactive metal oxides and metal oxide composites have shown promising results that may lead to designing practical catalysts for destruction and removal of such compounds [15,16]. As an example, high-surface area magnesium oxide coated with small amounts of iron Oxide has

Shown a remarkable catalytic oxidation activity toward carbon tetrachloride [17]. In another recent study, high-surface-area alumina was found to possess a remarkable catalytic potential for oxidation of chlorinated hydrocarbon (CHC) compounds in the presence of water [18].

Chlorinated hydrocarbons involve a wide range of organic compounds that have been produced and used in several applications. Fields of application include adhesives, pesticides, insecticides, fire retardants, detergents, and many others. Due to the hydrophobic character of these compounds, they accumulate in animal lipids, and as a result humans are exposed to a high intake of CHC especially from other animals such as sea animals where such compounds reach easily. As an example, DDT which was widely used in the seventies as a strong insecticide was found to accumulate in tissues and cause severe health damages. Other famous examples are polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) which form as by-products in industrial processes or by incinerations and are highly toxic and resistant to biodegradation. Chlorobenzenes represent other common examples which are used as intermediates in the synthesis of pesticides and other chemicals.

Hexachlorobenzene, HCB was used as a fungicide on grains, especially wheat. The release of chlorobenzenes to the environment occurs primarily during manufacture and through the dispersive nature of their uses. Chlorobenzenes tend to accumulate in tissues with a high fat content due to the lipophilic nature of these compounds. Their effects on the liver, kidneys, adrenal glands, mucous membranes, brain cells and metabolising enzymes have been observed.

Finally, other simpler CHCs, such as CCl_4, are produced and used in large amounts and have several hazardous effects especially the damage they cause to human liver. In this thesis, we chose to study and compare the behavior of copper oxide systems toward two CHC compound which are carbon tetrachloride and tetrachloroethylene.

1.7 Copper oxides in catalysis

The oxides of transition metals such as iron, nickel, cobalt, zinc, and cooper have many important applications. They are used, for example, in magnetic storage media, in solar energy transformation, as semiconductors in electronic devices, and as catalysts in a variety of important processes. Although precious metal catalysts are in general more active and also more tolerant to sulphur poisoning than metal oxides [19,20,21], metal oxides provide a range of other advantages. Metal oxides can be prepared as ultra fine powders that exhibit reactive surfaces toward a wide range of reactions. Besides their reactive surfaces metal oxides can be prepared in large amounts through cost-effective methods.

Away from its significant role in catalysis, copper(II) oxide has been studied as a semiconducting material for photoconductive and photothermal applications [22] The importance of CuO in catalysis and other applications can be associated with some of its unique characteristics including the natural abundance of starting material (Cu), the low-cost production processing, its non-toxic nature, and its reasonably good electrical and optical properties [21].

CuO composites such as CuO-ZnO and CuO-SnO systems have also been used in important applications such as in humidity and gas sensors [23,24,25,26]. Recent research efforts have shown that cupper (II) oxide and composites containing CuO are potential candidates as catalysts in several important processes including environmentally important reactions. Table 1.2 shows a brief summary of important reactions catalyzed by copper oxide-based catalysts.

Table 1.2 Reactions Catalyzed by CuO- based catalysts

The catalyst	Reactions(Processes)	Notes	References
CuO/ZrO_2	CO oxidation		27
CuO	Oxidation		28
CuO/CeO_2	CO oxidation, Reduction of NO with hydrocarbons, and Oxidation of methan	Reactivity is comparable to that of reactive metals	29 30 31
CuO/Al_2O_3	Complete oxidation of ethanol NO+CO reaction	More active than other transition metal oxides	33,31 34
CuO/MnO_2	Combustion of ethanol CO oxidation	Comparable to Pt/Al_2O_3	19,35

$CuO-Pd/La-Al_2O_3$	Oxidation of CO Oxidation of hydrocarbons		36
CuO	Synthesis of methanol		37

1.8 Preparation

1.8.1 Preparation of Pure CuO

Limited number of chemical methods have been reported to prepare pure CuO. The most common method is "forced precipitation" which is used to prepare several other transition metal oxides. In this method the starting precursor is an inorganic salt such as copper chloride or nitrate in an aqueous solution. Addition of a basic solution such as ammonium or sodium hydroxide results in the precipitation of copper hydroxide which can be converted thermally to copper oxide. Preparation of nanoscale particles of CuO was reported, where $CuCl_2$ in ethanol resulted in 7-9 nm particles of surface area around 120 m^2/g [37].

Pure CuO has been also prepared through solid state reactions. Uniform copper oxide in nanorods with average diameters of ca. 8 nm and lengths of up to 400 nm has been reported [38].

1.8.2 Preparation of Composites Containing CuO

1.8.2.1 Supported CuO by Wetness Impregnation:

The most common method to prepare supported catalysts including supported copper oxide has been the well established wet impregnation. This method involve the impregnation of the already-prepared solid support, such as another

oxide or porous carbon, with an aqueous solution of copper inorganic salt such as copper(II) nitrate. If the volume of the solution is calculated to just fill the pores of the support the method is referred to as incipient wetness impregnation. After impregnation, the composite is dried in air and is then treated at elevated temperatures [39,40,41].

The structure of the supported copper oxide species is usually dependent on the amount of CuO loaded. At low CuO loading, only a highly dispersed surface CuO species is formed on the support and when the CuO loading exceeds its dispersion capacity, crystalline CuO is formed. In the case of CuO/TiO_2 it has been found that both the reduction behavior and the crystalline structure of the TiO_2 support are related to the interactions between TiO_2 and CuO [42].

1.8.2.2 Supported CuO by Thermochemical Methods (Chemical Vapor Condensation):

Supported copper oxides have been prepared using various deposition techniques such as chemical vapour deposition, electro-deposition, thermal oxidation and sputtering process starting with a chemical precursor [34,43,44,45]. The precursor is usually vaporized and then oxidized. The rapidly condensed product particles are then deposited on a substrate. As an example, the chemical vapor deposition of 2,4-pentanedionate copper (II) as a precursor on fiberglass as substrate has been reported. The fiberglass coated with copper oxides showed a catalytic activity for the oxidation of ethanol into a stream of air at different temperatures [46].

Nanometer-sized metallic particles of Cu/SiO2 catalyst have been constructed

by spin coating copper (II) acetate {$Cu(CH3CO_2).H_2O$, $Cu(ac)_2$} solutions of different concentrations onto polished Si(100) substrates with an 5-10 nm SiO_2 oxide overlayer [47]. Homogenously distributed, nanometer-sized CuO particles were formed by calcinating the samples at 450 °C. Narrow particle size distributions were observed with mean particle size increasing with increasing the concentration.

Thin films of copper oxide have been also prepared using the various thin-film deposition techniques including chemical vapor deposition, thermal oxidation and sputtering process [34,35].

1.8.2.3 Oxidation of Cu particles:

Nanometer-sized CuO has been prepared within a support medium such as silica gel or alumina by controlled oxidation of copper nanoparticles [39].

Starting with 6.0 nm particles of copper, CuO shells of thickness between 1.1 and 1.7 nm have been made by heat treatment at temperatures between 450 and 850 °C.

1.8.2.4 CuO in an organic matrix via Sonochemical Method:

In several recent studies, a new class of crystallization modifiers have been developed and employed in the control of crystal morphologies. These modifiers are basically double hydrophilic block copolymers where one block interacts strongly with the mineral surface and the other block simply keeps the construction site in solution. As an example, uniformly dispersed copper oxide nanoparticles in poly(vinyl alcohol) have been synthesized by sonochemical methods starting with copper(II) acetate monohydrate [48].

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF THE CATALYSTS

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF THE CATALYSTS

2.1 Introduction

Due to their importance in several fields of application, metal oxides have received special attention from chemists as well as engineers in recent years. Several recent studies have shown that the physical as well as the chemical properties of metal oxides are strongly related to the method of their preparation. As a result, a great deal of recent research efforts have been exerted in the direction of discovering and exploring new ways to prepare metal oxides with highly reactive surfaces through cost effective methods for large scale applications.

It is now well established that materials made of nanoscale particles or crystallites exhibit unique properties and characteristics as compared with their bulk counterparts [1]. This has resulted in a considerable amount of research in an effort to prepare nanostructured metal oxides looking for new and unique catalytic potential as well as unique performance in several other applications. As we have mentioned in Chapter one, the most common method to prepare pure copper oxides has been through precipitation of copper hydroxide from aqueous solution of copper ions. Supported copper oxides have been obtained mainly by impregnation of a porous support by an aqueous solution of copper salt, such as copper nitrate or copper chloride, followed by heat treatment. In this chapter we

will discuss our attempts to prepare pure Copper (II) oxide by forced precipitation method in a variety of solvents including water and several alcohols. A comparison between aqueous and nonaqueous solvents will be discussed. Supported Copper(II) oxide on different supports have also been prepared and characterized.

2.2 Experimental

2.2.1 Chemicals

Copper(II) chloride (97% pure), aluminum isopropoxide ($[(CH_3)_2CHO]_3Al$, 99.99+%), tert-butanol (2-methyl-2-propanol, 99%), methanol (99.5%), copper(II) nitrate ($[Cu(NO_3)_2.2.5H_2O]$, 99%) and activated carbon were obtained from Aldrich. 2-propanol (99.5%), 1-butanol (99.5%), and 1-propanol were obtained from J. T. Baker. Ethanol (96%) was obtained from Alfa Acer. Commercial aluminum oxide (Al_2O_3) was obtained from Seasoul North America Inc. Titanium oxide (TiO_2) was obtained from Degussa. All chemical were used as received.

Sol-Gel alumina ($SG\text{-}Al_2O_3$) was prepared via sol-gel method. In a typical experiment, 5.0 g of $Al[OCH(CH_3)_2]_3$ was dissolved in 300 ml of 2-propanol with stirring for 30-50 minutes. 1.35 ml of H_2O was added drop wise to the solution with vigorous stirring during a period of about 30 minutes. The solution was stirred for more than 4 hours and then left standing for 24 hours for complete gelation after which the solvent was removed by drying in air for 14 days. The

white hydroxide powder obtained was dried at 120 °C for 2 hours and calcined for 5 hour at 500 °C for complete conversion to alumina.

2.2.2 Characterization Techniques and Instruments

FTIR spectroscopy was studied using a Nicolet FT-IR Magna-IR 560 and a Nicolet Nexus 470 FT-IR spectrometers. The systems are fully computerized using state-of-the-art software, Omnic. Samples were prepared for FTIR analysis as KBr/sample pellets (2% sample by wt). Transparent pellets were obtained by pressing the mixture using a hydraulic press. Spectra were recorded at room temperature by accumulating 32 scans at a spectral resolution of 4 cm^{-1} in the range of 400 to 4000 cm^{-1} and the spectrum of pure KBr was subtracted as a background.

Thermogravimetric Analysis (TGA) was carried out using a Thermogravimetric Analysis, TA Instrument, GA 2950. Samples weighing around 10 mg were heated in a ceramic sample boat to 900 °C at 10 °C/min in a stream (40 ml/min) of nitrogen gas.

BET surface area measurements were obtained using nitrogen gas adsorption at 77 K employing a Quantochrome Autosorb-1 volumetric gas sorption instrument. Prior to measurements, all samples were outgassed for 1 hour at 150°C to remove physisorbed water.

Powder X-ray diffraction (XRD) patterns were obtained using a Philips PW1840 diffractometer at room temperature. Ni-filtered Cu-Kα radiation (λ= 0.15418 nm)

was employed. The patterns obtained were compared with standard JCPDS cards for identification.

2.2.3 Preparation of Pure Copper(II) Oxide

Pure CuO was prepared through forced precipitation starting with Cu(II) nitrate, $Cu(NO_3)_2.2.5(H_2O)$ or Cu(II) chloride, $CuCl_2$. A variety of solvents have been employed as shown in Table 2.1. In a typical experiment, for example in methanol, 4.5g of $Cu(NO_3)_2.2.5H_2O$ was dissolved in 250 mL methanol with continuous stirring giving a blue solution. A separate solution of 1.5g of NaOH dissolved in 200 mL methanol was prepared and then added to the first solution slowly while stirring. The mixture was stirred for two more hours. A blue precipitate formed which was filtered out after 24 hours and washed with doubly distilled water. The precipitate was further washed in a beaker containing 100 mL of distilled water for 10 minutes and then filtered again. Finally the blue product, which was characterized by FTIR and powder XRD to be $Cu(OH)_2$, was dried for 2 hours at 120 °C in an oven where the color turned black. Complete conversion of the hydroxide product was achieved by calcination at temperatures above 250 °C for 3 hours.

Table 2.1 shows a summary of the observations from other preparations where the same procedure discussed above was employed. Starting with $CuCl_2$, the same procedure was also used. The color of the initial precipitate varied from blue-greenish (hydroxide) to black (oxide). The samples prepared were labeled A1-7

for those prepared from the chloride precursor and B1-7 for those prepared from the nitrate precursor.

Table 2.1 A summary of the observations from the different preoperational experiments of pure CuO.

Precursor	**Solvent**	**Precipitate Color**	**Color change**	**Label**
$CuCl_2$	Methanol	Greenish-blue	turned black upon drying	A1
$CuCl_2$	Ethanol	Black	-	A2
$CuCl_2$	1-Butanol	Greenish-blue	turned black upon drying	A3
$CuCl_2$	Water	Blue	turned black upon drying	A4
$CuCl_2$	t-Butanol	green	Turned black upon air drying	A5
$CuCl_2$	Isopropa-nol	green	turned black upon drying	A6

$CuCl_2$	1-Propanol	Greenish-blue	turned black upon drying	A7
$Cu(NO_3)_2.2.5H_2O$	Methanol	Blue	turned black after drying	B1
$Cu(NO_3)_2.2.5H_2O$	Ethanol	Blue	turned black upon washing	B2
$Cu(NO_3)_2.2.5H_2O$	1-butanol	Greenish-blue	turned brownish during washing	B3
$Cu(NO_3)_2.2.5H_2O$	Water	Blue	turned black upon air drying	B4
$Cu(NO_3)_2.2.5H_2O$	Tert-butanol	blue		B5
$Cu(NO_3)_2.2.5H_2O$	Isopropanol	Greenish-blue	-	B6
$Cu(NO_3)_2.2.5H_2O$	1-propanol	Greenish-blue	turned black after washing	B7

2.2.4 Preparation of Supported Copper Oxide Catalysts

CuO supported on the surface of other high-surface-area materials has been prepared using the well established wet impregnation method. The supporting materials employed in this study included commercial TiO_2, activated carbon, and the sol-gel-prepared alumina, SG-Al_2O_3. Some characteristics of supporting materials are summarized in Table 2.2.

Table 2.2 Some Characteristics of the Supporting Materials

Support	Source	Specific Surface Area (m^2/g)	Total Pore volume (cc/g)
SG-Alumina	Prepared	211	1.3
TiO_2	Degussa	50	0.5
Activated Carbon	Aldrich	499	-

In all supported catalysts the CuO loading was 4%. CuO was supported on alumina and by incipient wetness impregnation, where the appropriate amount of $Cu(NO_3)_2.2.5H_2O$ was dissolved in enough water just to fill the pores of the support. The solution was added drop wise to the powder. The impregnated powder was then dried in an oven at 120 °C followed by calcinations at 500 °C for 5 hours. In the case of activated carbon and titania supports, only wetness impregnation was employed where the nitrate precursor was dissolved in the

maximum amount of solvent that could be absorbed by the support sample. In the case of titanium oxide-supported samples, 0.61 g of $Cu(NO_3)_2.2.5H_2O$ was dissolved in 2.5 ml of doubly distilled H_2O. The aqueous solution was added drop by drop to 5.0 g of TiO_2 which was then mixed well before drying and calcination. For the alumina-supported catalyst, 0.61 g of $Cu(NO_3)_2.2.5H_2O$ dissolved in 5.6 ml of H_2O was added to 5 g of alumina giving a paste-like mixture. The same procedure was used in the case of activated carbon using 0.61 g of $Cu(NO_3)_2.2.5H_2O$ dissolved in 7.0 ml of H_2O and 5.0 g carbon was used.

2.3 Results and Discussion

The two main objectives of the work discussed in this chapter are: First, to prepare pure CuO with high surface area. To achieve this goal, a variety of alcoholic solvents and water were employed and compared. The second goal was to prepare reactive supported copper oxide where the copper oxide will be highly dispersed on the surface of other high-surface-area supports.

2.3.1 Preparation of Pure CuO

Generally, the solvated Cu(II) ions in water result in the release of the acidic hydrogen of the complexing water molecules as H^+ in the solution. This process results in condensation of the soluble species and eventually may lead to precipitation. Similar behavior is expected in alcoholic solvents. This behavior was indicated by the significant drop in the pH of the solutions upon dissolving the Cu precursor but no precipitation was observed. Precipitation started only after

the addition of NaOH where the OH^- ions abstract the acidic hydrogens from the coordinated solvent molecules allowing for condensation and precipitation. The observed blue precipitate indicates that this process readily results in the formation of $Cu(OH)_2$ (blue) precipitate in water. On the other hand, alcoholic solvents, studied here, generally resulted in greenish-blue precipitate, especially from the chloride precursor. This greenish precipitate converted to the blue hydroxide or black oxide readily upon washing or oven drying (see table 2.1). It is likely that the greenish color is due to the presence of some alcoholic molecules within the lattice of the hydroxide. This is supported by the fact that the greenish color was not observed in water and was observed less often using the hydrated nitrate precursor. The presence of water in the nitrate precursor leads to complete hydrolysis resulting in the hydroxide formation. The objective of studying various solvent systems was to compare between the aqueous and the alcoholic solvents, especially in relation to surface areas, which will be discussed below.

2.3.2 BET (Brunauer-Emmet-Teller) Surface Areas of Pure Copper Oxide

BET surface area of samples was measured for the products after oven drying (120 °C) and after calcination at 250 °C as shown in Table 2.3. For selected samples, surface area was measured after calcinations at different temperatures as shown in

Table 2.4. Generally, it has been noticed that alcoholic solvents resulted in relatively higher surface areas than water. Among the alcohols studied, ethanol and t-butanol seemed to result in products of higher surface areas (122-133 m^2/g) than other alcohols. Upon calcination at 250 °C, the surface areas dropped to the range of 20-60 m^2/g (Table 2.3). Comparing the results from the chloride and the nitrate precursors, there was no significant difference except that the decrease in the surface area due to calcination was more pronounced in the products from the nitrate precursor especially in the cases of sample B3 and B4. Although this part of the work was not investigated further and definitely more work is needed to extract more solid conclusions, we can conclude that preparation in ethanol or t-butanol is more likely to result in smaller particles and higher surface areas of copper oxide. It is possible that the higher surface areas of the products form alcohols as compared with water are due to the fact the initial soluble species, which eventually resulted in the precipitate, was not pure hydroxide as indicated by the greenish color. It is likely that it contained Cu-OR bonds besides the Cu-OH. This may have limited the condensation process which usually results from the release of water molecules from the initial soluble product. It can be also concluded that chloride precursor resulted in, generally, higher surface areas for the 250 °C-calcined CuO. Again, more work is needed in this direction but in the rest of this thesis we will focus on the reactivity of the prepared pure and supported CuO toward selected chlorinated hydrocarbons.

Table 2.3 BET Specific Surface Area (SSA) of Pure CuO Prepared in Different Solvents.

Precursor	Label	SSA (m^2/g)	
		Drying at 120 °C	Calcination at 250 °C
$CuCl_2$	A1	49.2	22.0
	A2	133.2	39.1
	A3	67.0	38.7
	A4	52.0	38.4
	A5	122.0	62.0
	A6	61.0	17.0
	A7	88.0	26.7
$Cu(NO_3)_2.2.5H_2O$	B1	86.4	17.0
	B2	128.5	28.7
	B3	51.0	8.5
	B4	26.0	9.1
	B5	33.0	30.4
	B6	76.0	51.5
	B7	44	32.2

A2 and B2 samples were calcined at different higher temperatures for 4 hours and their specific surface areas were measured after each heat treatment as shown in Table 2.4. Their FTIR spectra and Powder X-ray diffraction patterns were also recorded as will be discussed in the coming sections. As one may expect, the surface area decreased as the samples were heated at elevated temperatures which

is a commonly known behavior due to sintering. As we have discussed above and as indicated from the TGA study (will be discussed below), complete conversion to oxide can be achieved by heating at temperatures between 180-250 °C, where the surface area can be preserved in the range of 40-60 m^2/g.

Table 2.4 BET Specific Surface Area of Selected Pure CuO Samples After Calcination at Different Elevated Temperatures.

Sample	Specific Surface Area (m^2/g) vs. Calcination Temperature		
	250 °C	300 °C	400 °C
A2	39.12	31.43	19.41
B2	28.69	24.21	17.6

2.3.3 FTIR Characterization of Pure CuO

FTIR spectra were recorded for the various samples upon drying and after calcinations at 250 °C. For A2 and B2 samples, FTIR spectra were recorded after calcination at higher temperatures. The FTIR spectra of products from all preparations were basically similar. The spectra showed the typical spectrum reported for pure CuO with main absorption peaks at 435, 529, 599 cm^{-1} representing νCu-O (Figure 2.1). For products obtained after drying at 120 °C, the spectra contained absorption bands between 3200 and 3600 cm^{-1} which are due to

ν(OH) of the hydroxide and some adsorbed water as indicated by the deformation band of water at 1629 cm^{-1}. They also contain weak absorption peaks between 2850 and 3000 cm^{-1} which are due to organic residues form the solvent. Upon calcination, the broad band centering at ~3400 cm^{-1} decreased showing the conversion of the hydroxide product to oxide which was found by TGA analysis, as will be discussed later, to take place largely at around 200 °C. At higher temperatures, >300 °C, the remaining band in this region and the peak at 1629 cm^{-1} must be due to surface adsorbed water, due exposure to air. Also, the band at 435 cm^{-1} decreased in intensity upon heating which may suggest that it refers to surface Cu-OH groups which are removed as a result of heating and sintering (Figure 2.1).

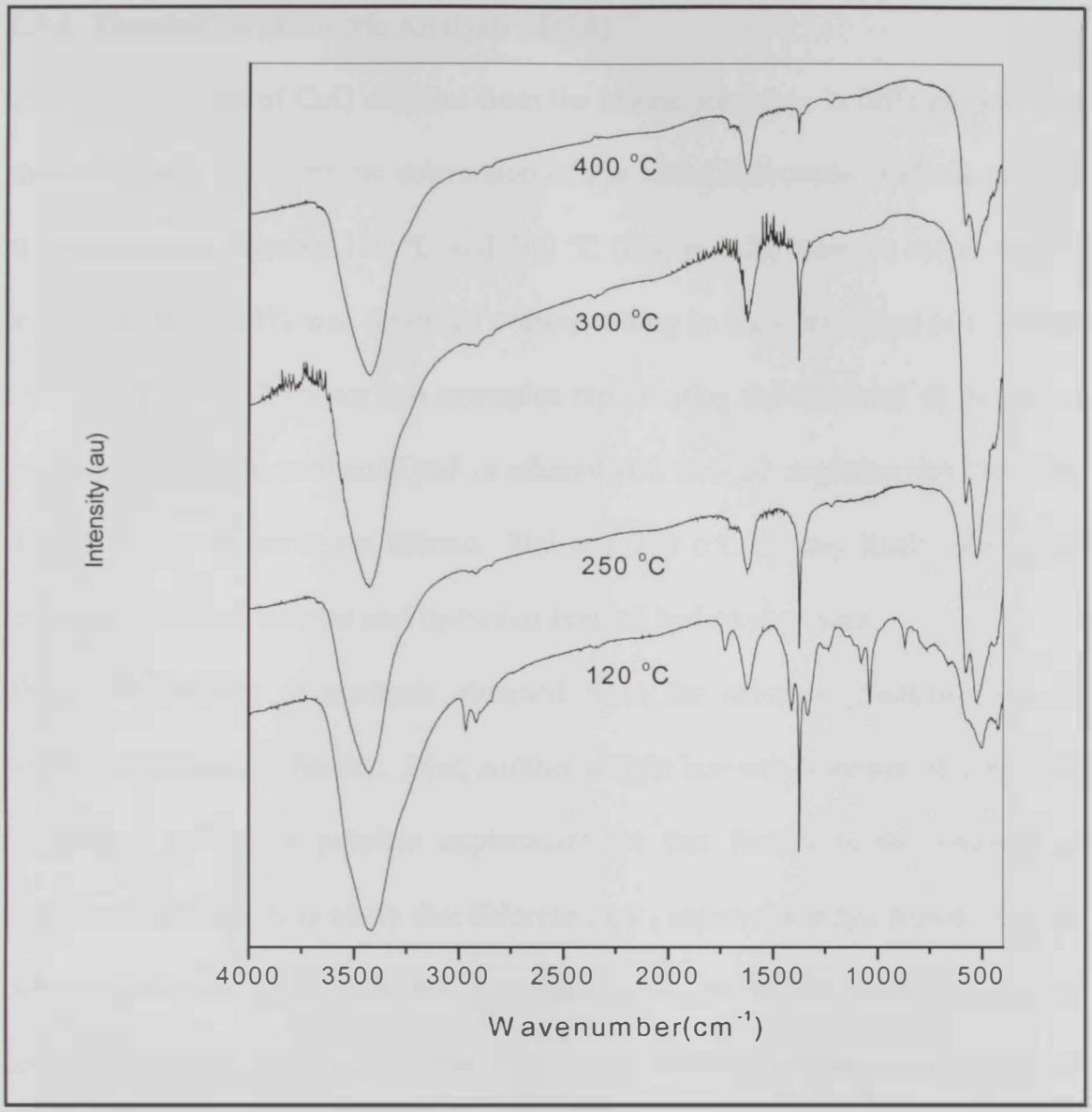

Figure 2.1 FTIR spectra of B2 sample after drying at 120 ºC and calcinations different temperatures.

2.3.4 Thermal Gravimetric Analysis (TGA)

The TGA analysis of CuO samples from the nitrate precursor in different solvents showed clearly the complete conversion of the initial hydroxide products to CuO at temperatures between 180 °C and 200 °C (Figure 2.2), where a major weight loss of about 12-15% was observed corresponding to the conversion of $Cu(OH)_2$ to CuO. Figure 2.2 shows two examples representing the behavior of the initial product obtained in methanol and in ethanol (B1 and B2 respectively).The slow weight loss at temperatures between 200 and 350 o C is very likely due to the removal of surface isolated and hydrogen-bonded hydroxyl groups.

The TGA analysis of products obtained from the chloride precursor showed somewhat different behavior. First, another weight loss was observed at about 400 °C (Figure 2.2). One possible explanation for this feature is the removal of coordined chloride. It is likely that chloride ions , especially when present in high concentration, compete with the hydroxide ions, which are present in lower concentration, and coordinate to the copper ions. Besides the removal of coordined chloride, decomposition of organic residues may contribute to this feature. Second, the products from the chloride precursor showed, generally, conversion to oxide at relatively higher temperature (220-270 °C). Although these differences are still not well understood, they are significant in optimizing the preparational procedure as will be discussed later in this chapter.

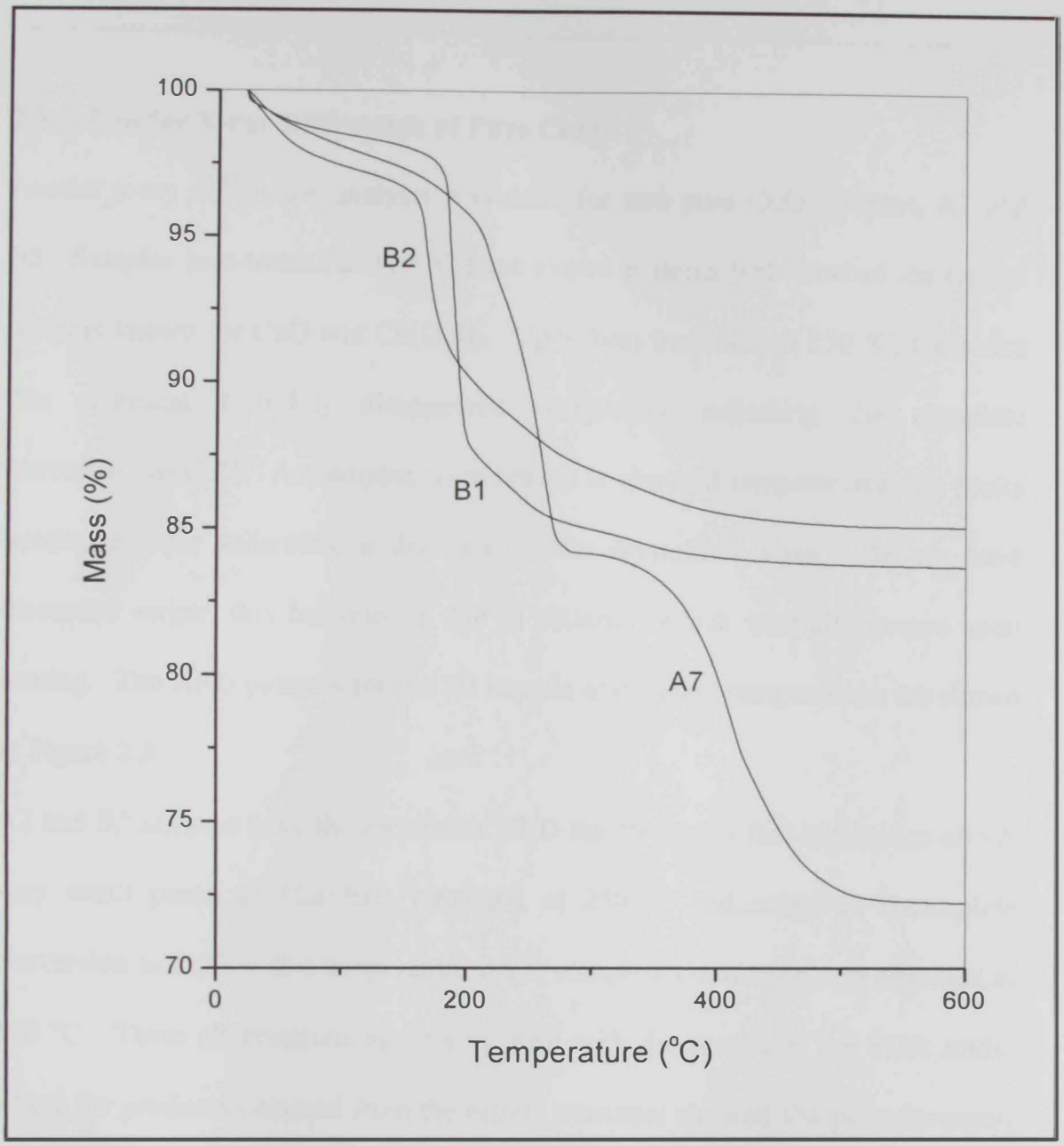

Figure 2.2 TGA analysis of B1, B2, and A7 samples.

2.3.5 Powder X-ray Diffraction of Pure CuO

Powder x-ray diffraction analysis was done for two pure CuO samples, A2 and B2. Samples heat-treated at 120 °C have shown patterns that matched the typical patterns known for CuO and $Cu(OH)_2$. Upon heat treatment at 250 °C, the peaks that represent $Cu(OH)_2$ disappeared completely indicating the complete conversion to CuO. As samples were heated at elevated temperatures, the peaks became sharper indicating a decrease in the crystallites sizes. As we have discussed earlier, this behavior is due to sintering which normally occurs upon heating. The XRD patterns for the B2 sample at different temperatures are shown in Figure 2.3.

A2 and B2 samples have shown similar XRD results except that in the case of A2, very small peaks of $Cu(OH)_2$ remained at 250 °C indicating an incomplete conversion to CuO at this temperature while complete conversion was observed at 300 °C. These observations agree very well with the results of the TGA study, where the products obtained from the nitrate precursor showed sharper conversion to CuO at temperatures around 190 °C. These resluts suggest that the nitrate precursor has an advantage over the chloride precursor since the nitrate resulted in the pure CuO at a lower temperature where the surface area can be better preserved.

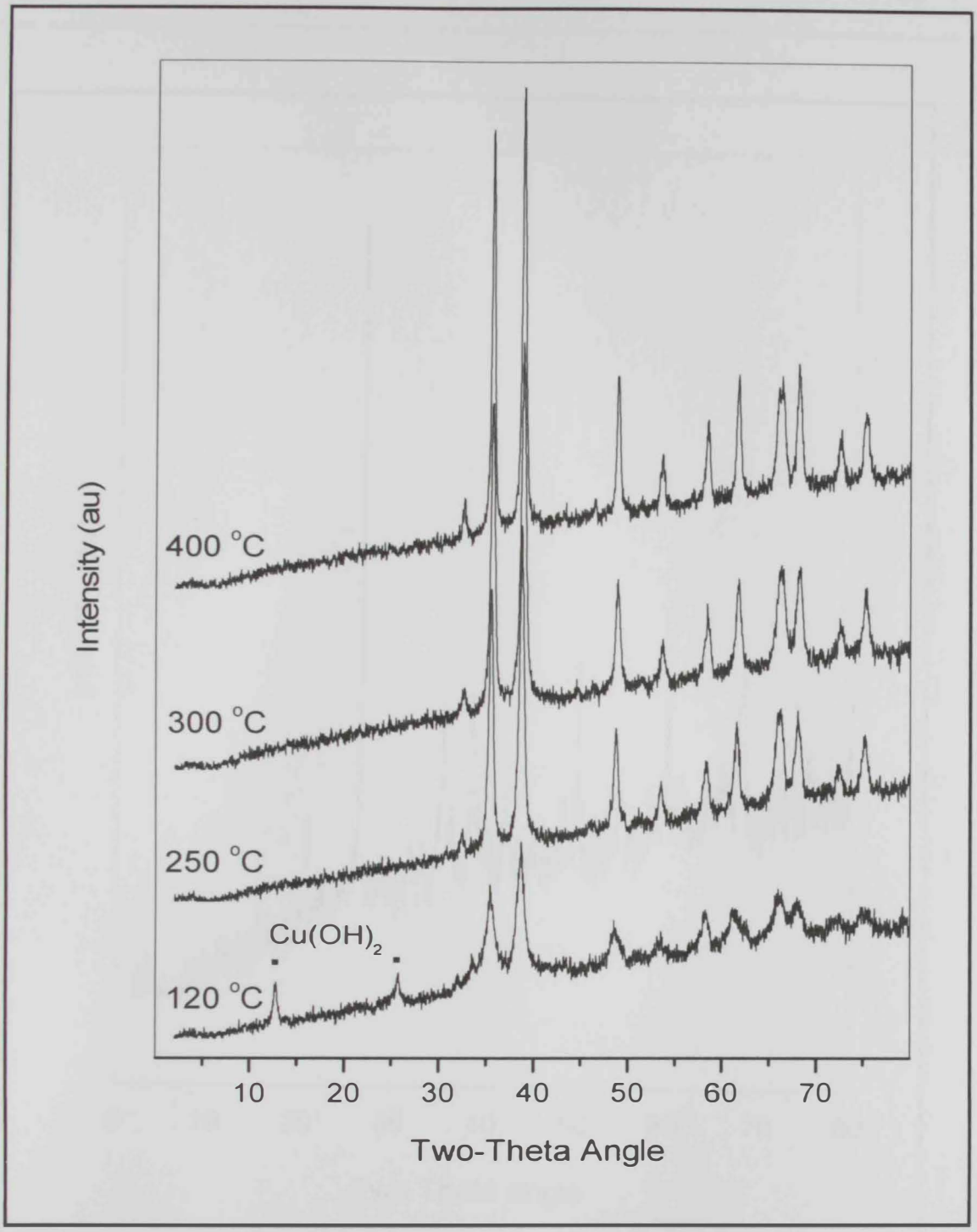

Figure 2.3 Powder XRD patterns for pure CuO (B2 sample) calcined at different temperatures.

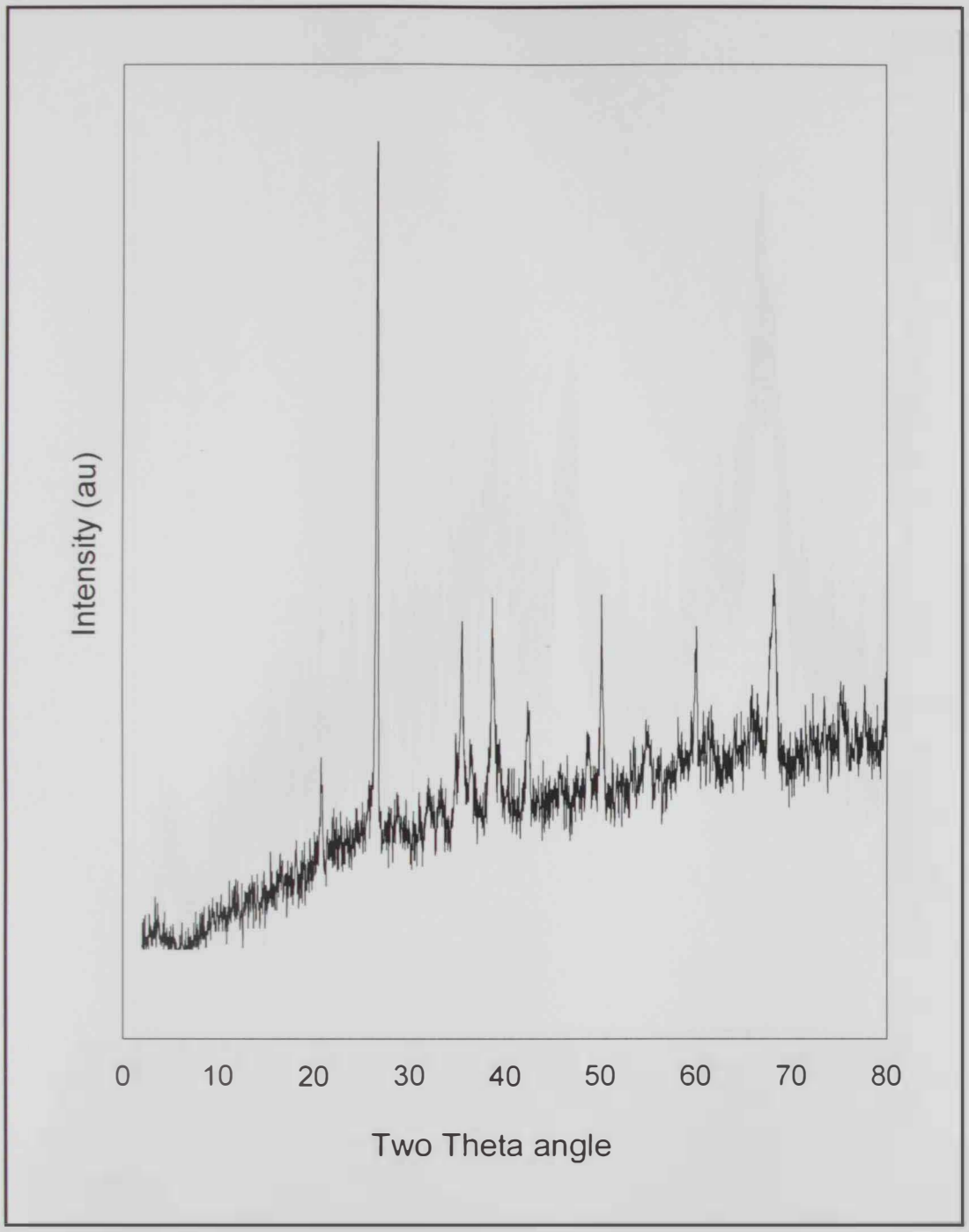

Figure 2.4 Powder x-ray diffraction pattern of CuO/C

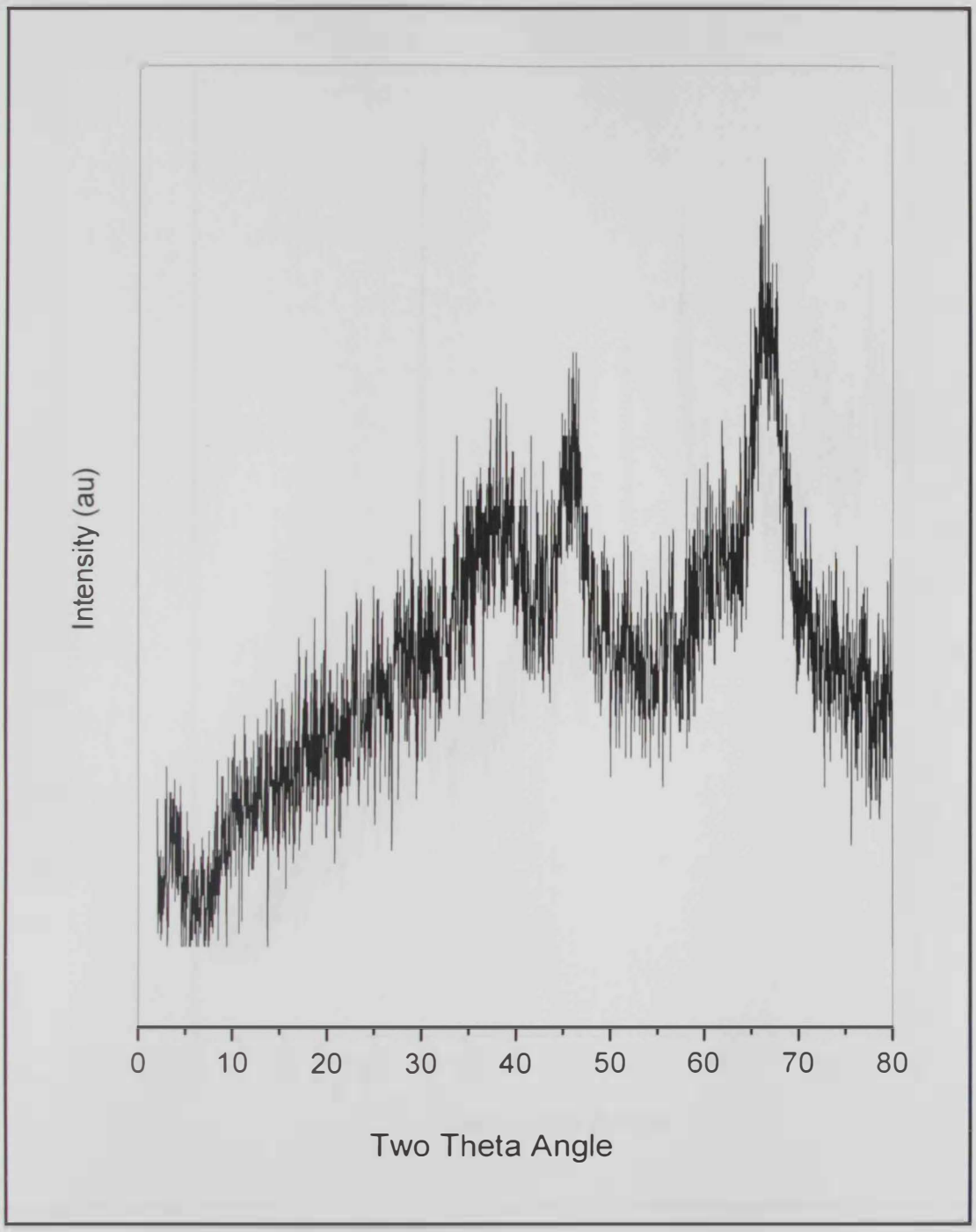

Figure 2.5 Powder x-ray diffraction pattern of CuO/Al_2O_3

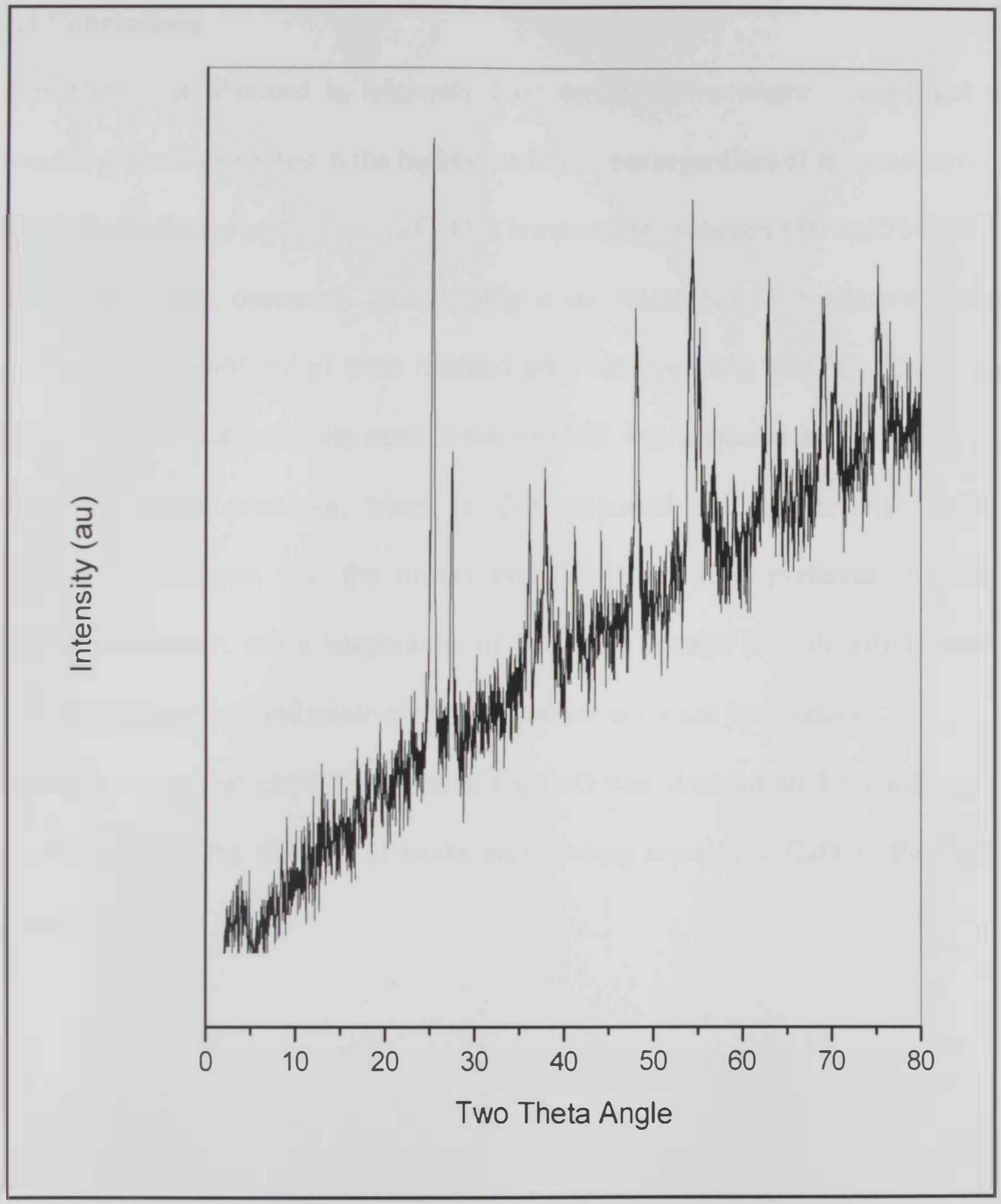

Figure 2.6 Powder x-ray diffraction pattern of CuO/TiO_2

2.4 Conclusions

Pure CuO was obtained in relatively high surface areas where ethanol and t-butanol generally resulted in the highest surface areas regardless of the precursor. $Cu(OH)_2$ converted completely to CuO at temperatures between 180 and 250 °C. The surface area decreased considerably upon calcination, but relatively high surface areas (40-60 m^2/g) were retained after calcination at 250 °C. The TGA study showed that complete conversion to CuO was achieved at about 200 °C using the nitrate precursor, which is also supported by XRD results. These observations suggest that the nitrate precursor should be preferred over the chloride precursor, and a temperature of 200 °C is enough for calcination where complete conversion and relatively higher surface areas can be obtained.

Finally,it seems that good dispersion of the CuO was obtained on TiO_2 and Al_2O_3 as indicated by the absence of peaks representing crystalline CuO in the XRD patterns.

CHAPTER THREE

THE REACTIVITY OF THE COPPER OXIDE CATALYSTS TOWARD THE DECOMPOSITION AND THE HYDROLYSIS OF CARBON TETRACHLORIDE AND TETRACHLOROETHYLENE.

CHAPTER 3

The reactivity of the copper oxide catalysts toward the decomposition & the hydrolysis of carbon tetrachloride & tetrachloroethylene

3.1 Introduction

Chlorinated hydrocarbon compounds (CHC) are among a series of volatile organic compounds that are toxic and are emitted in the environment from different sources as discussed in chapter 1. They have shown a wide range of toxic effects on human and the environment in general. The widely used method to decompose large amounts of these compounds has been incineration, which is usually accompanied by the formation of a range of toxic gases including polychlorinated dibenzodioxins [1-3]. The environmental problems associated with incineration and the fact that CHC compounds exist in air and in water in low concentrations make the need for new technologies to treat and remove such compounds from the environment very essential. Several recent studies have shown that one of the promising methods to remove these compounds is adsorption by powders and catalytic decomposition. Reactive metal oxides and metal oxide composites have exhibited significant reactivity toward some simple CHC compounds but in most of the systems that have been reported, other stable CHC compounds form as side products such tetrachloroethylene, C_2Cl_4 and $COCl_2$ [4-6]. As a result, more new sorbents and catalytic systems should be investigated searching for systems that lead to more complete decomposition and minimum unwanted side products. In this chapter we discuss and compare the results of our study on the reactivity of pure copper (II) oxide and supported

copper (II) oxide toward the decomposition of C_2Cl_4 and CCl_4 in the presence and the absence of water.

3.2 Experimental

3.2.1 Chemicals and Instruments

CCl_4 (99.9% pure) and C_2Cl_4 (99%) were purchased from Aldrich and used as received. Distilled deionized water was used in all reactions. The catalysts investigated included CuO, TiO_2, carbon, and TiO_2-, C-, and SG-Al_2O_3-supportd CuO. The preparation of SG-Al_2O_3 and the catalysts characterization is described in chapter 2. FTIR spectra of the gaseous products of all reactions were recorded on a Nicolet Nexus 470 FT-IR spectrometer. Powder X-ray diffraction (XRD) analyses of the catalysts after reactions were obtained using a Philips PW/1840 diffractometer with Cu-K_α radiation.

3.2.2 Catalytic Reactions: Setup and Experimental Procedure

The catalytic reactions were studied using FTIR spectroscopy employing a fixed-bed flow reactor system (Figure 3.1). In a typical experiment, 0.125 g of the catalyst in study was placed in a U-shaped Pyrex tube (6 mm diameter) reactor and heated (10 degrees/minute) under He flow (20 mL/minute) to the process temperature. A cylindrical heater around the reactor was used and the temperature was monitored by a temperature controller and a K-type thermocouple placed close to the sample. The CHC reagent was injected in pulses along with the desired amount of water (when used) into the carrier gas stream in the heated zone

of the reactor. For FTIR analysis of the gaseous products, fixed amounts of the eluting gases after each pulse were transferred into a pre-evacuated gas IR cell equipped with KBr windows (Figure 3.2). The transfer line connecting the reactor and the IR cell was maintained at ~ 150 °C using a heating tape. 10–μL pulses of the reagent in study were injected every 10 minutes and FTIR spectra were recorded for the gaseous products after each pulse. The % conversion was calculated based on peak area measurement and comparison with spectra obtained from background experiments where no catalyst was used.

In some chosen experiments, the eluting gas stream was allowed to bubble in a trap containing 3.0 mL of potassium iodide aqueous solution (1.5 M) where Cl_2, if formed, would oxidize the iodide to iodine which is indicated by the brown color of the solution. The iodine was titrated with 0.05 M aqueous solution of sodium thiosulfate to determine the amount of chlorine. The amount of HCl produced was determined by titrating the same solution with 0.5 M NaOH. In some cases, the solid after reaction was characterized by XRD.

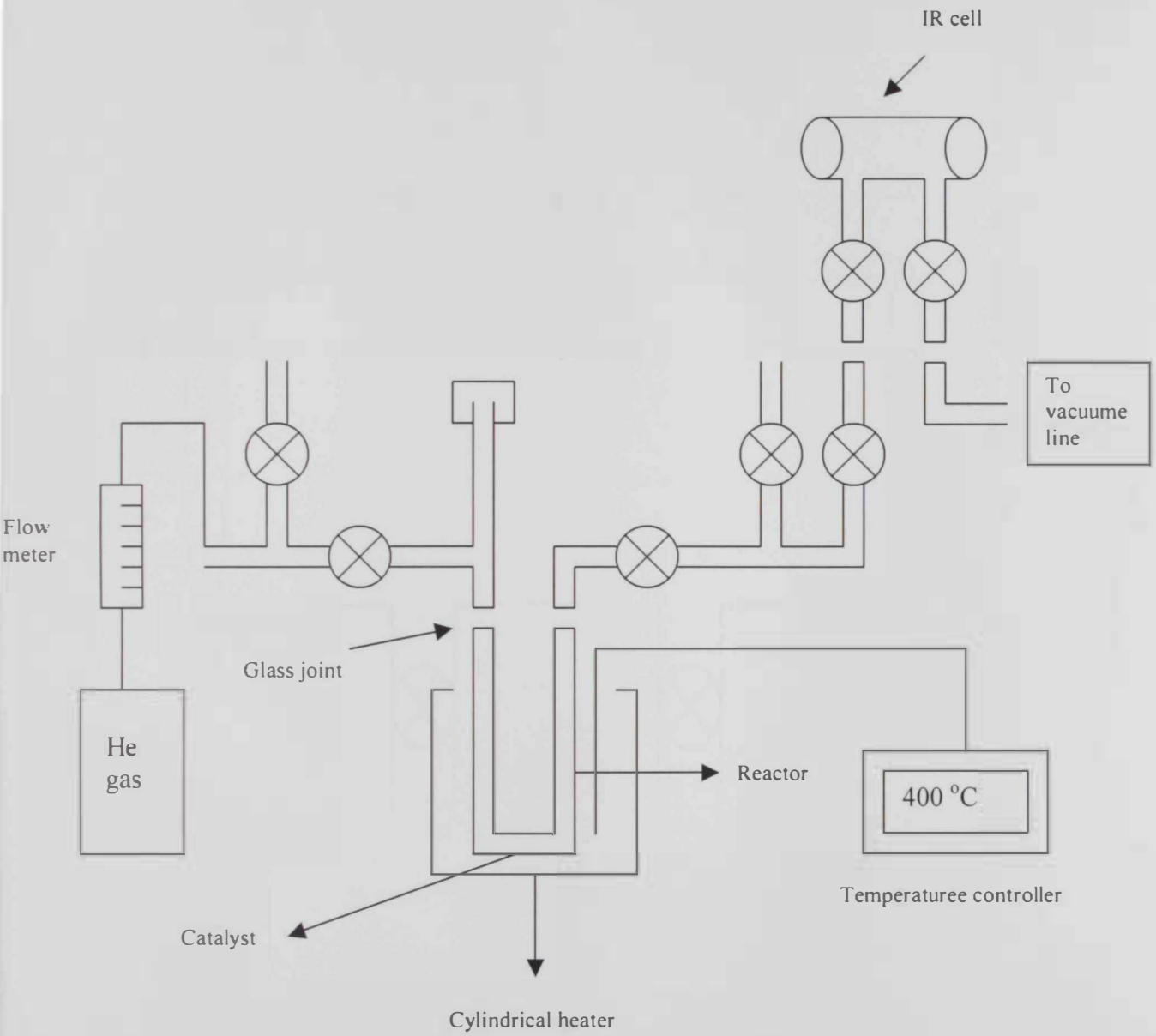

Figure 3.1 A scheme of the setup used in the catalytic reactions study.

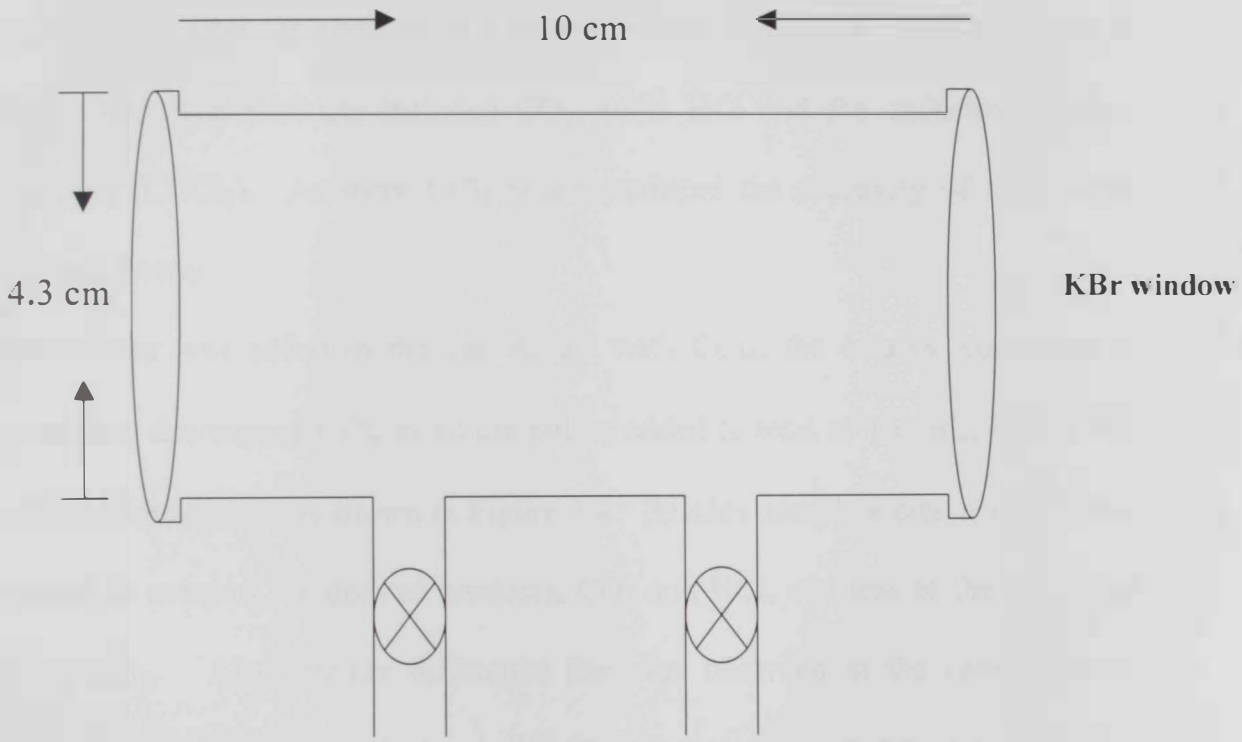

Figure 3.2 A scheme of the gas FTIR cell employed.

3.3 Results and Discussion

3.3.1 Decomposition and Hydrolysis of CCl_4 over Al_2O_3-CuO at 400 °C

In the absence of water, the alumina-supported copper oxide samples have shown some reactivity toward the adsorption and decomposition of CCl_4. In the first four pulses (10 μL each) about 85% conversion of CCl_4 was obtained which declined to about 60% after the addition of a total of 60 μL (6.21×10^{-4} mol) as shown in Figure 3.3. The products included CO_2, some HCl and the undesired product phosgene ($COCl_2$). As more CCl_4 was introduced the reactivity of the sample declined slowly.

When water was added in the gas stream with CCl_4, the catalyst continued to completely decompose CCl_4 in all the pulses added (a total of 100 μL, 1.04×10^{-3} mol, was introduced) as shown in Figure 3.4. Besides complete conversion, water resulted in more of the desired products, CO_2 and HCl, and less of the undesired gas, $COCl_2$. Also another difference that was observed in the case of water presence is the formation of traces of C_2Cl_4. For comparison, two corresponding spectra, one from each study, are shown in Figure 3.5.

From these results it is obvious that water plays a significant role in this process where it results in complete hydrolysis of CCl_4 to CO_2 and HCl. In another study on pure alumina [7], similar results were reported and it was proposed that the surface hydroxyl groups are the reactive species on the surface which results in

catalytic hydrolysis of CCl_4 to CO_2 and HCl. The addition of water increases the concentration of these sites which explains the high reactivity and the type of products formed. In the next section we will look at the same process on C-supported CuO and after comparison with the alumina supported samples, general conclusions will be drived.

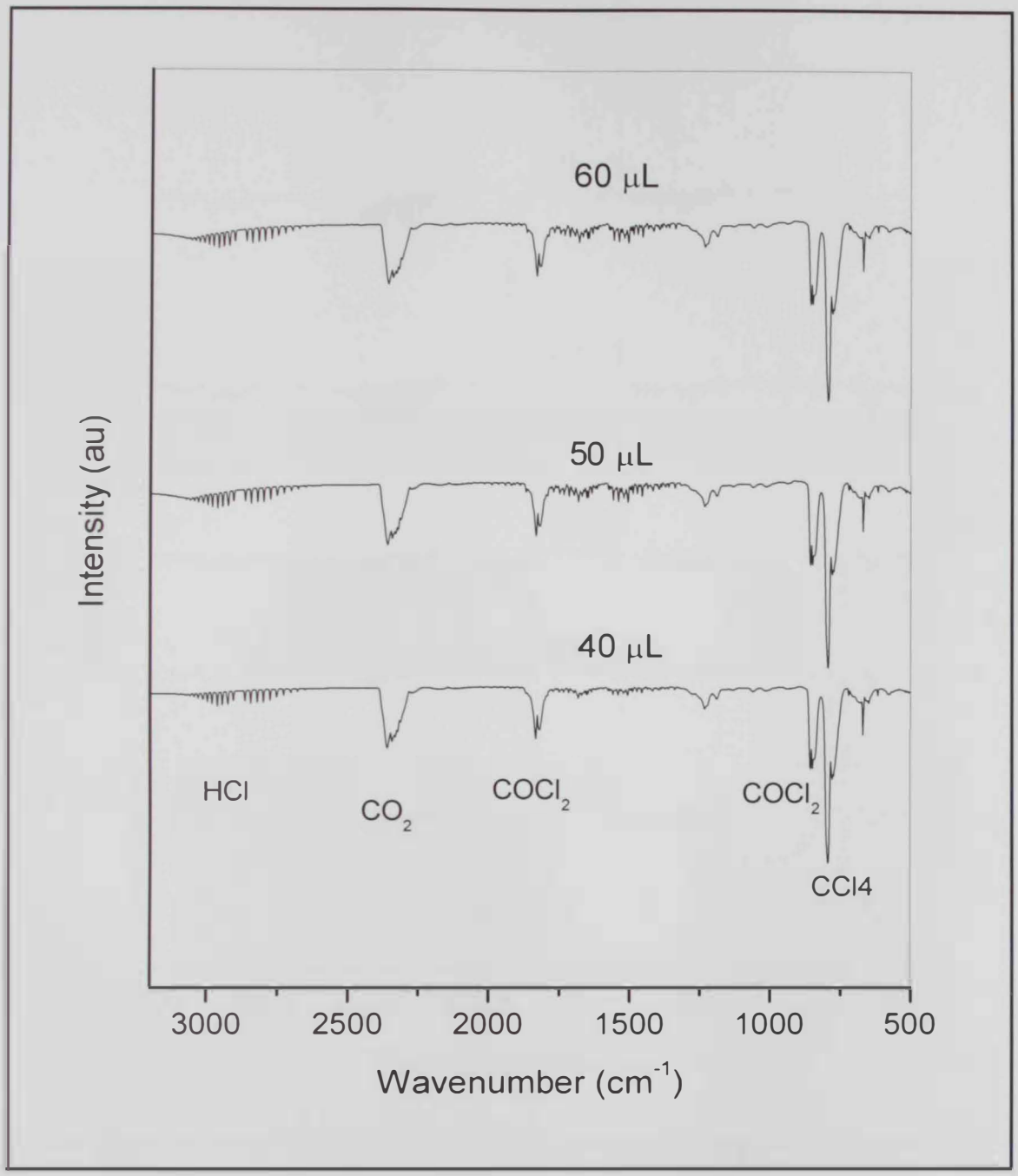

Figure 3.3 FTIR spectra of the gaseous products of the decomposition of CCl_4 over Al_2O_3-CuO at 400 °C in the absence of water.

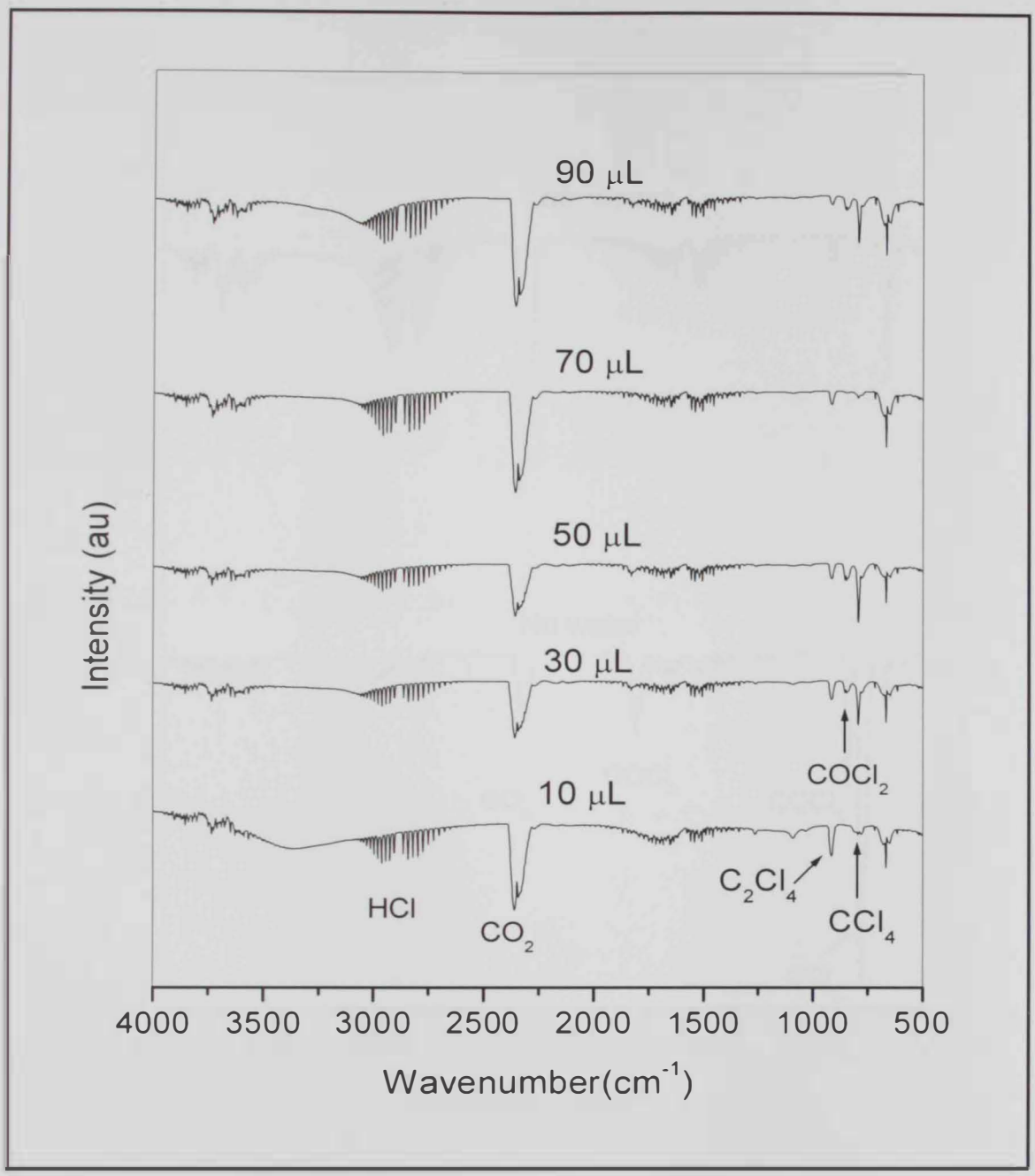

Figure 3.4 FTIR spectra of the gaseous products of the decomposition of CCl_4 over Al_2O_3-CuO at 400 °C in the presence of water.

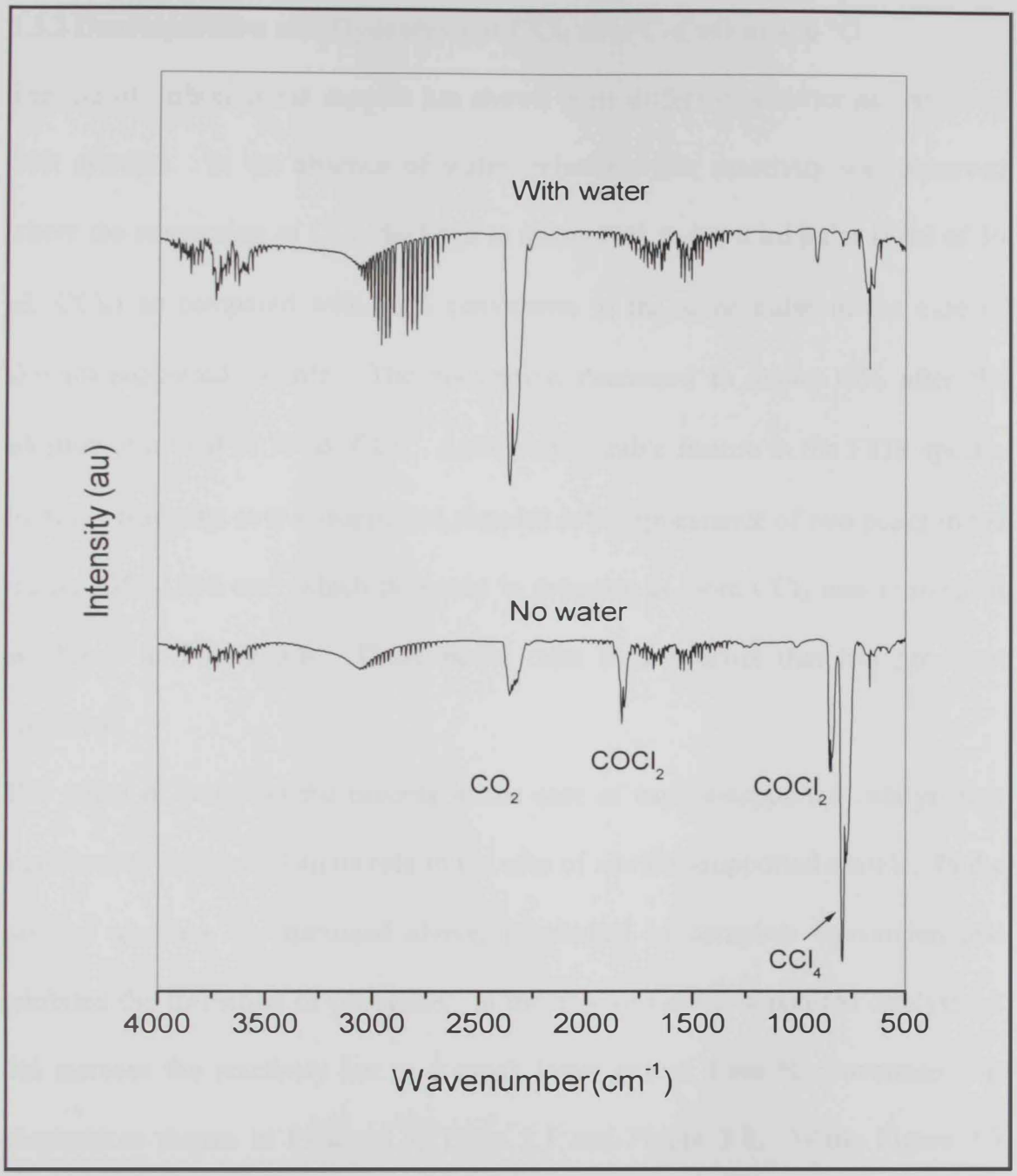

Figure 3.5 The presence vs. the absence of water in the CCl_4 decomposition over Al_2O_3-CuO. FTIR spectra of the gaseous products after the addition of a total of 70 μL CCl_4.

3.3.2 Decomposition and Hydrolysis of CCl_4 over C-CuO at 400 °C

The use of carbon as the support has shown quite different behavior as compared with alumina. In the absence of water, relatively low reactivity was observed where the conversion of CCl_4 declined to about 40% in the third pulse (total of 30 μL CCl_4) as compared with 85% conversion in the same pulse in the case of alumina-supported sample. The conversion decreased to about 15% after the addition of a total of 70 μL CCl_4. Another noticeable feature in the FTIR spectra from the reactions over C-supported samples is the appearance of two peaks in the region 1350-1390 cm^{-1} which deceased in intensity as more CCl_4 was introduced as shown in Figure 3.6. These peaks refer to a product that has not been identified.

The effect of water on the process in the case of carbon-supported catalyst was significantly different than its role in the case of alumina-supported sample. In the case of alumina, as discussed above, it resulted in complete conversion and inhibited the formation of phosgene. In the case of carbon-supported catalysts, it did increase the reactivity but to a much lesser extent. Less % conversion was obtained as shown in Figure 3.7, Table 3.1 and Figure 3.8. While Figure 3.7 shows the FTIR spectra of the gaseous products at different pulses from the reaction over carbon-supported catalyst, Table 3.1 and Figure 3.8 show the % conversion of CCl_4 at different pulses over both catalysts, alumina- and carbon-supported CuO.

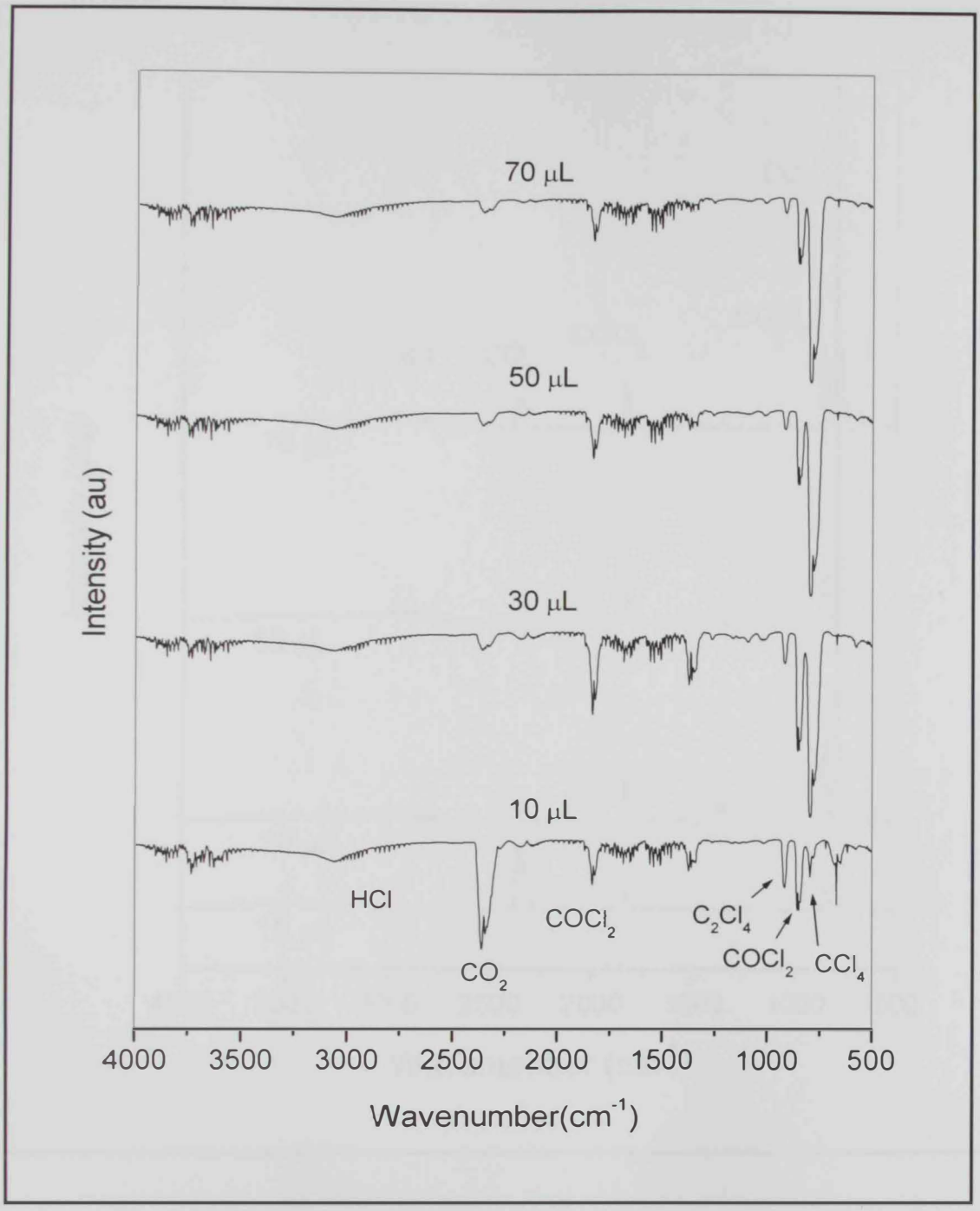

Figure 3.6 FTIR spectra of the gaseous products of the decomposition of CCl_4 over C-CuO at 400 °C in the absence of water.

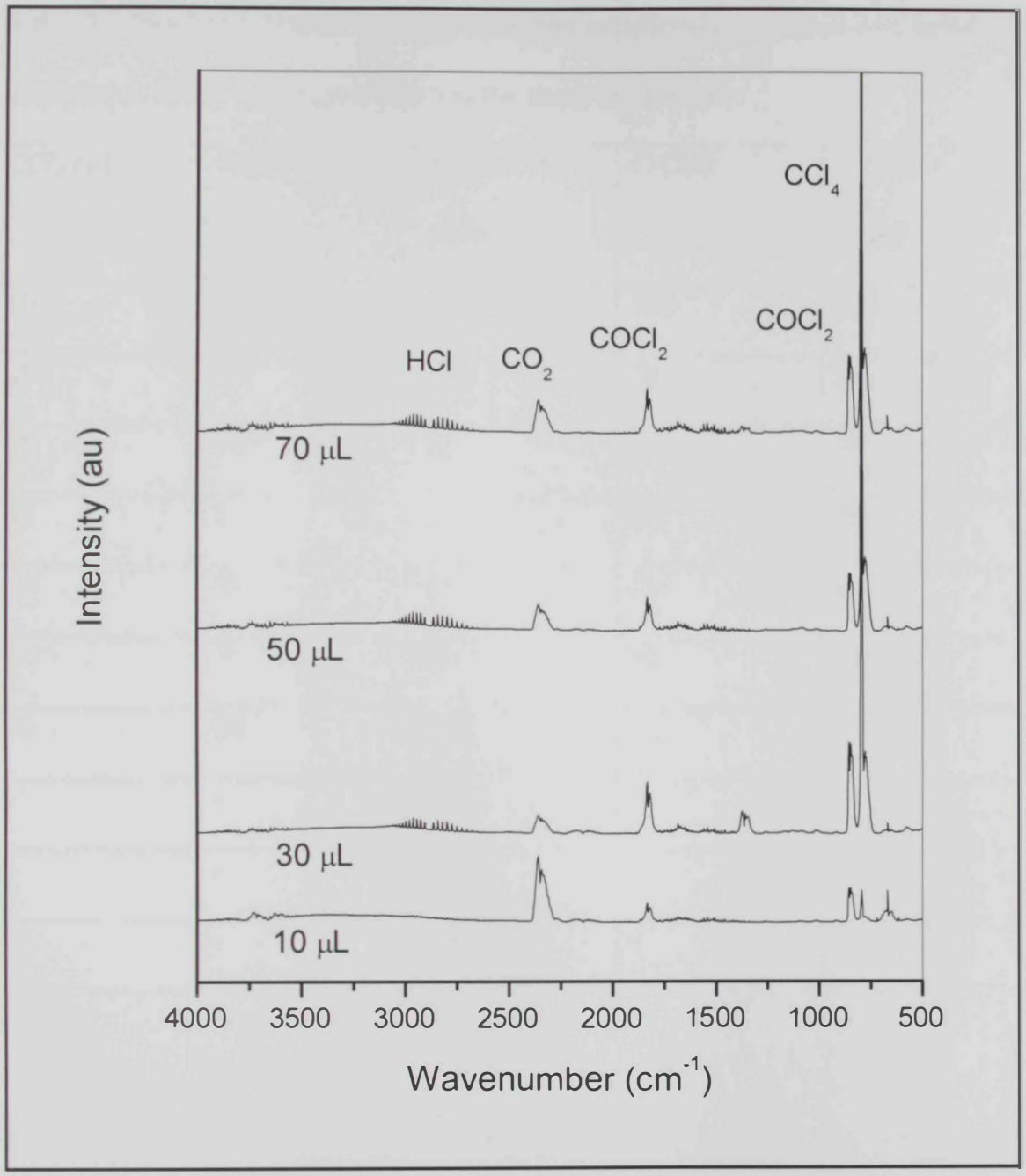

Figure 3.7 FTIR spectra of the gaseous products of the decomposition of CCl_4 over C-CuO at 400 °C in the presence of water.

Table 3.1 % Conversion of CCl_4 over alumina-supported and carbon-supported catalysts at 400 °C in the presence and the absence of water.

CCl_4 (μL)	Al_2O_3-CuO	Al_2O_3-CuO + water	C-CuO	C-CuO + Water
10	90	100	100	100
20	82	100	78	95
30	84	99	42	70
40	81	97	26	70
50	90	99	25	64
60	71	99.5	21	55
70	60	100	17	57
-	-	100	-	-
-	-	99	-	-
-	-	100	-	-

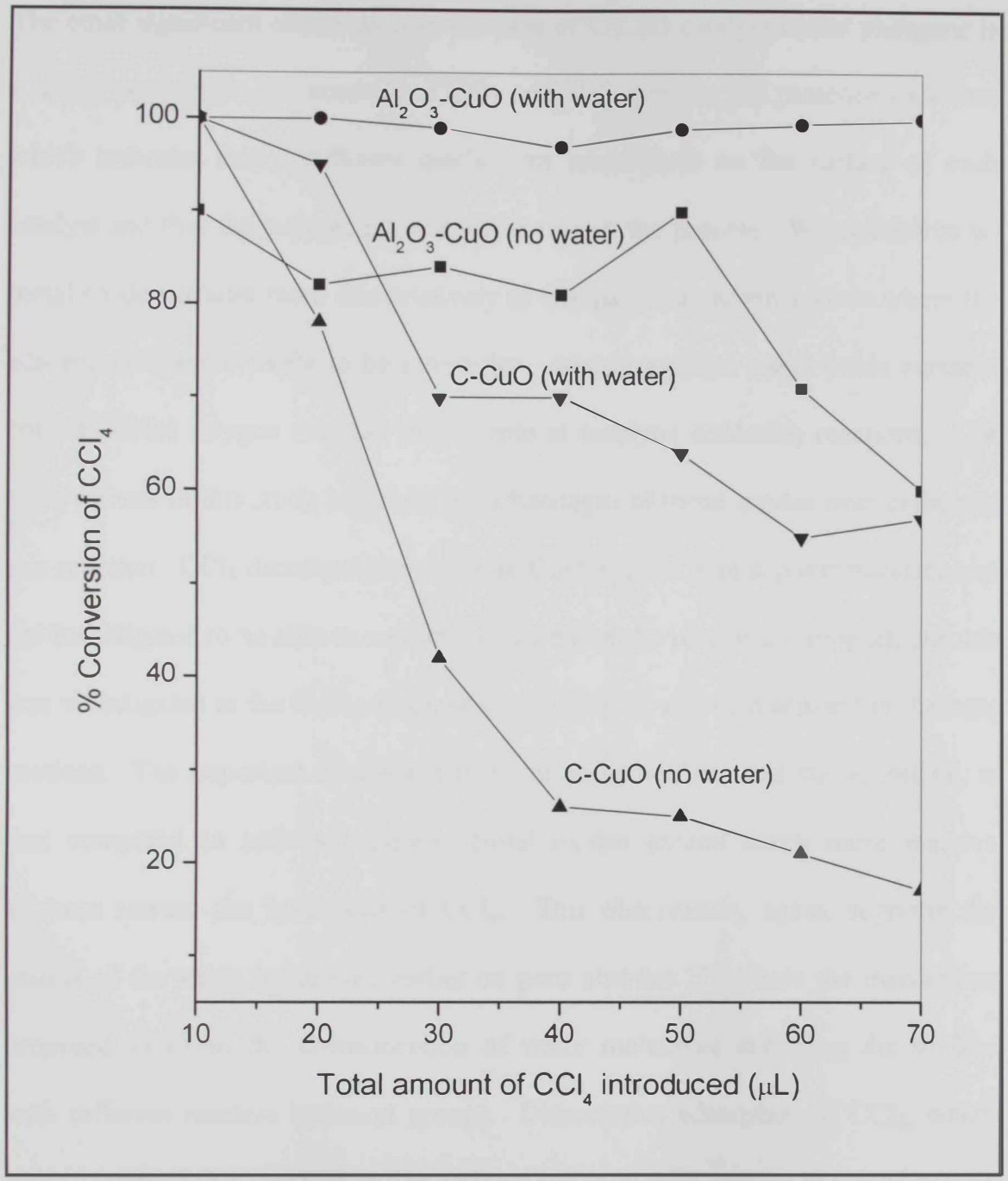

Figure 3.8 the % conversion of CCl_4 over alumina-supported and carbon-supported catalysts at 400 °C in the presence and the absence of water.

The other significant observation in the case of C-CuO catalyst is that phosgene is a major product on the account of CO_2 and HCl even in the presence of water, which indicates that a different mechanism takes place on the surface of each catalyst and that the support plays a major role in the process. Water adsorbs on metal oxide surfaces more dissociatively as compared to carbon surface where the adsorption is more likely to be molecular. Also, transition metal oxide surfaces contain lattice oxygen that can play a role in catalytic oxidation reactions. The observations in this study highlight the advantages of metal oxides over carbon in this reaction. CCl_4 decomposition by pure CuO and the pure support material was not investigated to be able to confirm the extent of the role of the support, but this was investigated in the C_2Cl_4 decomposition study as will be discussed in the next sections. The important conclusion that can be made from this study, though, is that compared to activated carbon, metal oxides exhibit much more reactive surfaces toward the hydrolysis of CCl_4. This observation, again, supports the results of the study mentioned earlier on pure alumina [7] where the mechanism proposed involved the chemisorption of water molecules enriching the surface with different reactive hydroxyl groups. Dissociative adsorption of CCl_4, which gives adsorbed CCl_2 species, followed by interaction with surface hydroxyl groups results in complete hydrolysis to CO_2 and HCl. The presence of excess water regenerates such hydroxylated surface. It is also interesting that CO was not

observed in significant amounts as compared to other similar studies reported in the literature [8,9].

3.3.3 Decomposition and Hydrolysis of C_2Cl_4 over pure CuO

C_2Cl_4 has shown higher stability toward sorption and decomposition by metal oxides. It has been observed as a byproduct from the decomposition of other CHC compounds such as CCl_4 as discussed above. Pure copper oxide, calcined at 250 °C, has shown some reactivity toward the adsorption and decomposition of C_2Cl_4 in the absence of water at 400 °C. Its reactivity is comparable with that of TiO_2 in the presence of water as will be discussed below. In contrast to the decomposition of CCl_4 over pure and supported catalysts, very small amount of HCl and no $COCl_2$ formed. The major product observed was CO_2. This indicates the absence of the hydrolysis effect from surface hydroxyl groups as was observed in the reactions of CCl_4. The observed reactivity, which is shown in Figure 3.9 in terms of % conversion, is relatively low as compared with that of supported catalysts which will be discussed in the coming sections.

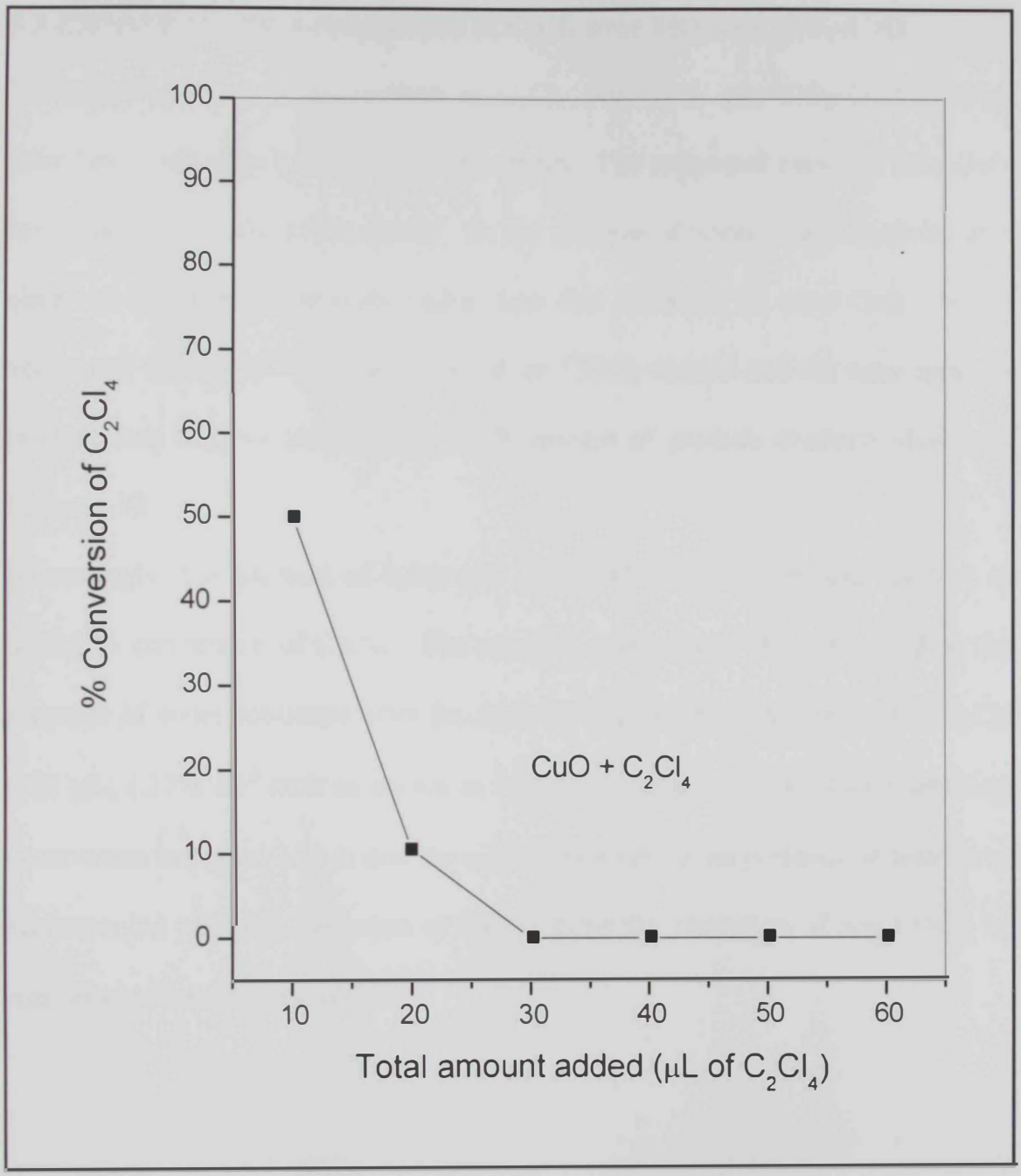

Figure 3.9 the % conversion of C_2Cl_4 in the absence of water over pure CuO (B2 sample) at 400 °C.

3.3.4 Hydrolysis and decomposition of C_2Cl_4 over TiO_2 and TiO_2-CuO

The hydrolysis and decomposition of C_2Cl_4 over TiO_2 and TiO_2-CuO systems have been studied in more details than others. The supported catalyst, TiO_2-CuO has shown some interesting results. In the absence of water some reactivity was observed which was relatively higher than that observed for pure CuO. While very small amount of HCl was observed, no $COCl_2$ formed and the main gaseous product was CO_2 as indicated by FTIR spectra of gaseous products shown in Figure 3.10.

Interestingly, the addition of water has enhanced the reactivity and resulted in higher % conversion of C_2Cl_4. The catalytic reactivity of the TiO_2-CuO in the presence of water continued after the addition of relatively large amount of C_2Cl_4 (120 μL, 1.17 x 10^{-3} mol) as shown in Figure 3.11 and 3.12. Another interesting observation in Figure 3.11 is that the higher reactivity in the presence of water was accompanied with the formation of HCl without the formation of any $COCl_2$ as was observed in the case of CCl_4.

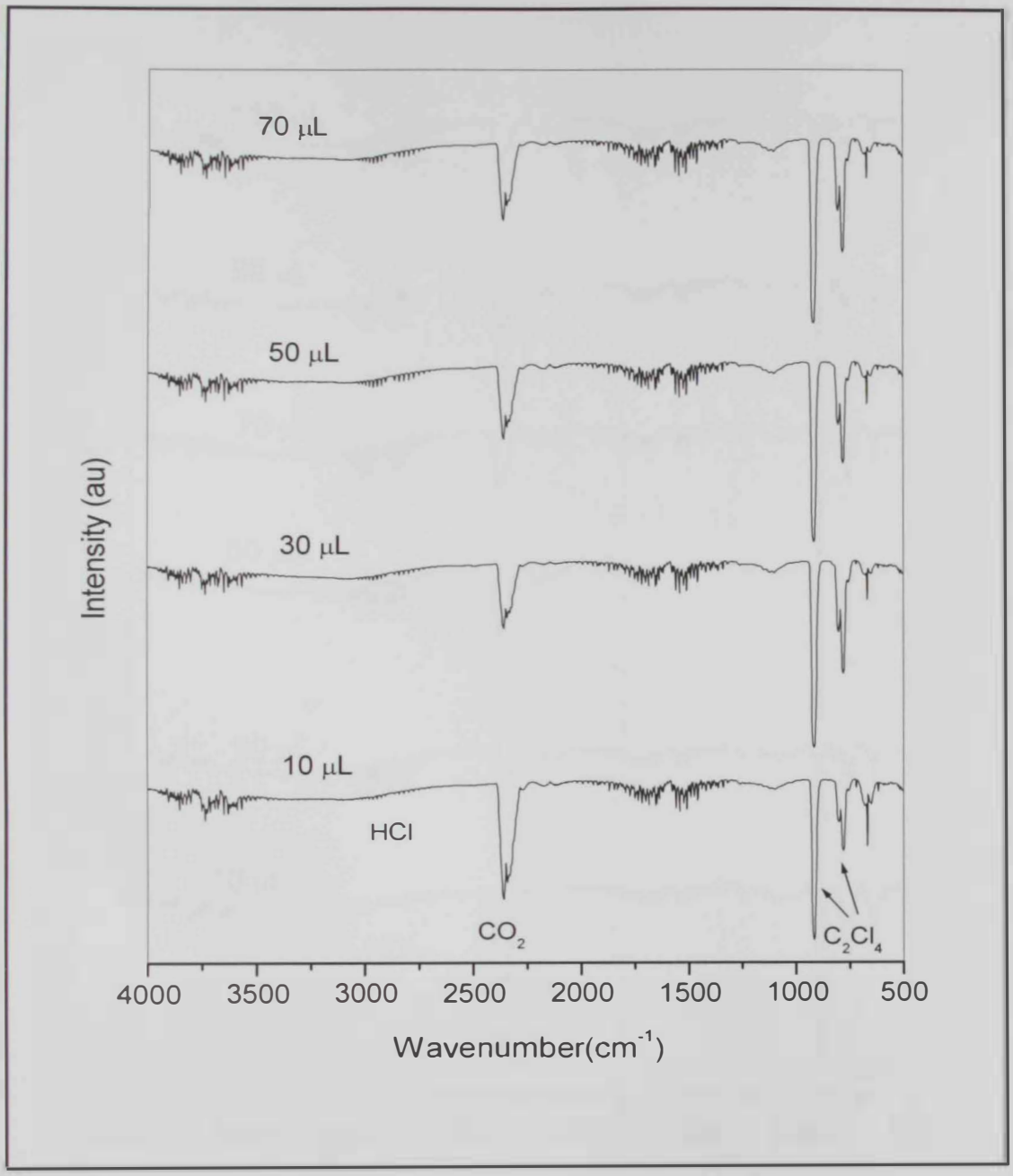

Figure 3.10 FTIR spectra of the gaseous products of the decomposition of C_2Cl_4 over TiO_2-CuO at 400 °C in the absence of water.

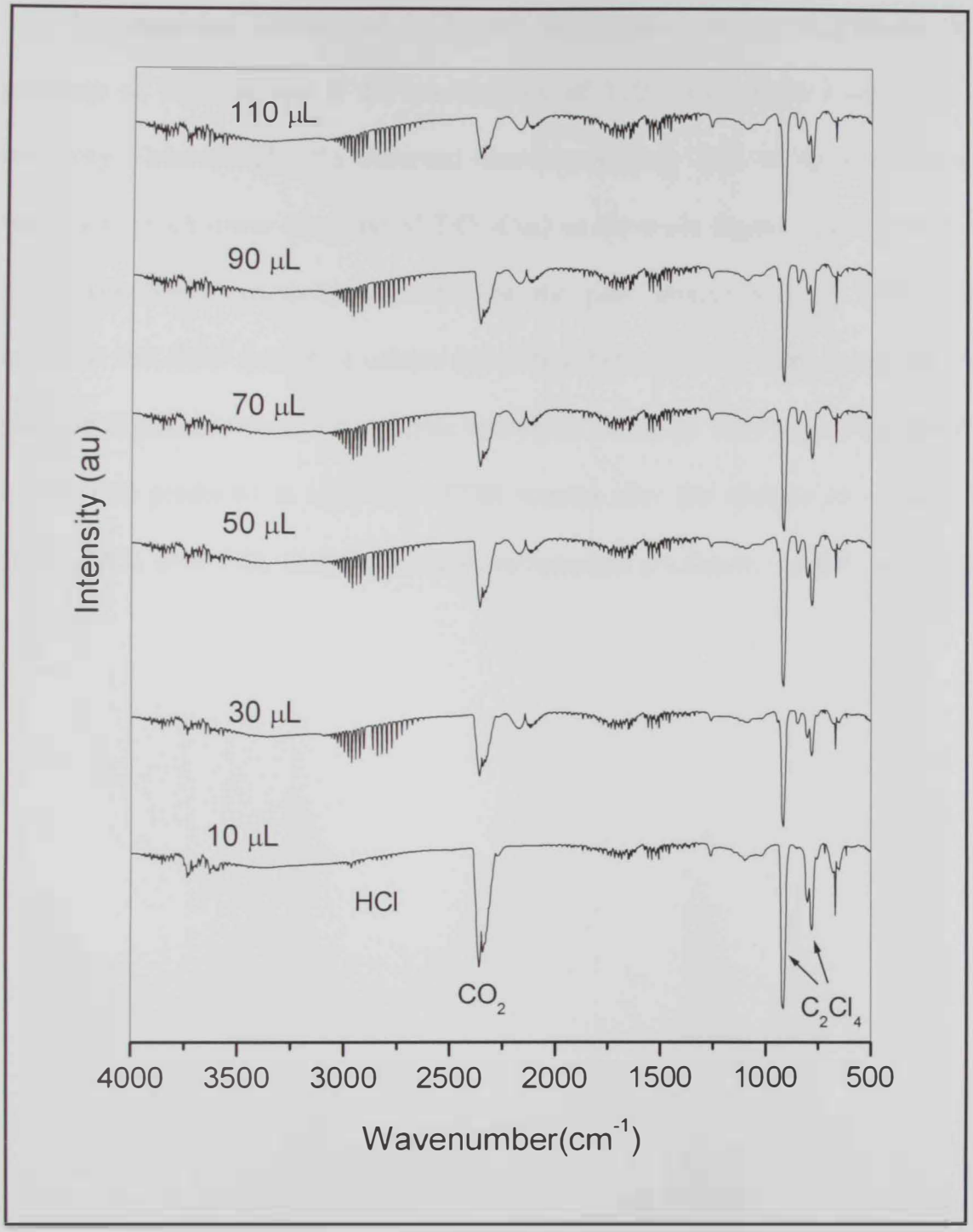

Figure 3.11 FTIR spectra of the gaseous products of the decomposition of C_2Cl_4 over TiO_2-CuO at 400 °C in the presence of water.

The decomposition reaction of C_2Cl_4 was also studied over pure TiO_2 in the presence of water to see if the combination of TiO_2-CuO exhibits any unique reactivity. Interestingly, the observed reactivity of pure TiO_2 in the presence of water was much lower than that of TiO_2-CuO as shown in Figure 3.12 and Table 3.2. The lower reactivity observed for the pure components of TiO_2-CuO confirms that there must be a unique interaction between both components which plays an important role in the catalytic hydrolysis of C_2Cl_4. To compare the nature of products produced in each case, FTIR spectra after the addition of a total of 50 μL C_2Cl_4 over TiO_2-CuO and its pure components are shown together in Figure 3.13.

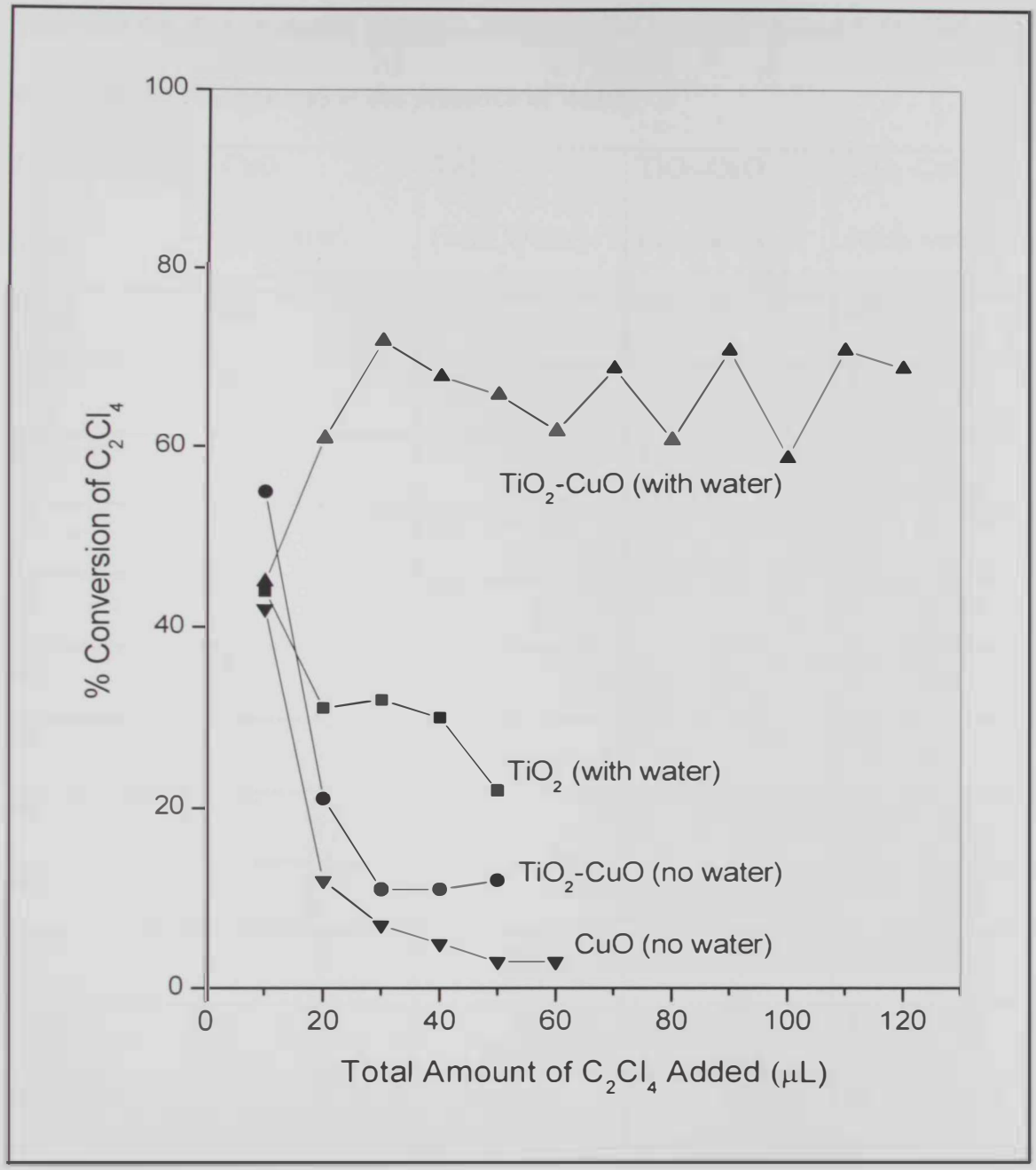

Figure 3.12 The % conversion of C_2Cl_4 over pure CuO, pure TiO_2 and TiO_2-CuO at 400 ºC in the absence and in the presence of water.

Table 3.2 The % conversion of C_2Cl_4 over pure CuO, pure TiO_2 and TiO_2-CuO at 400 °C in the absence and in the presence of water

Total C_2Cl4 (μL)	CuO (no water)	TiO_2 (with Water)	TiO_2-CuO (no water)	TiO_2-CuO (with water)
10	42	44	55	45
20	12	31	21	61
30	7	32	11	72
40	5	30	11	68
50	3	22	12	66
60	3	-	-	62
70	-	-	-	69
80	-	-	-	61
90	-	-	-	71
100	-	-	-	59
110	-	-	-	71
120	-	-	-	69

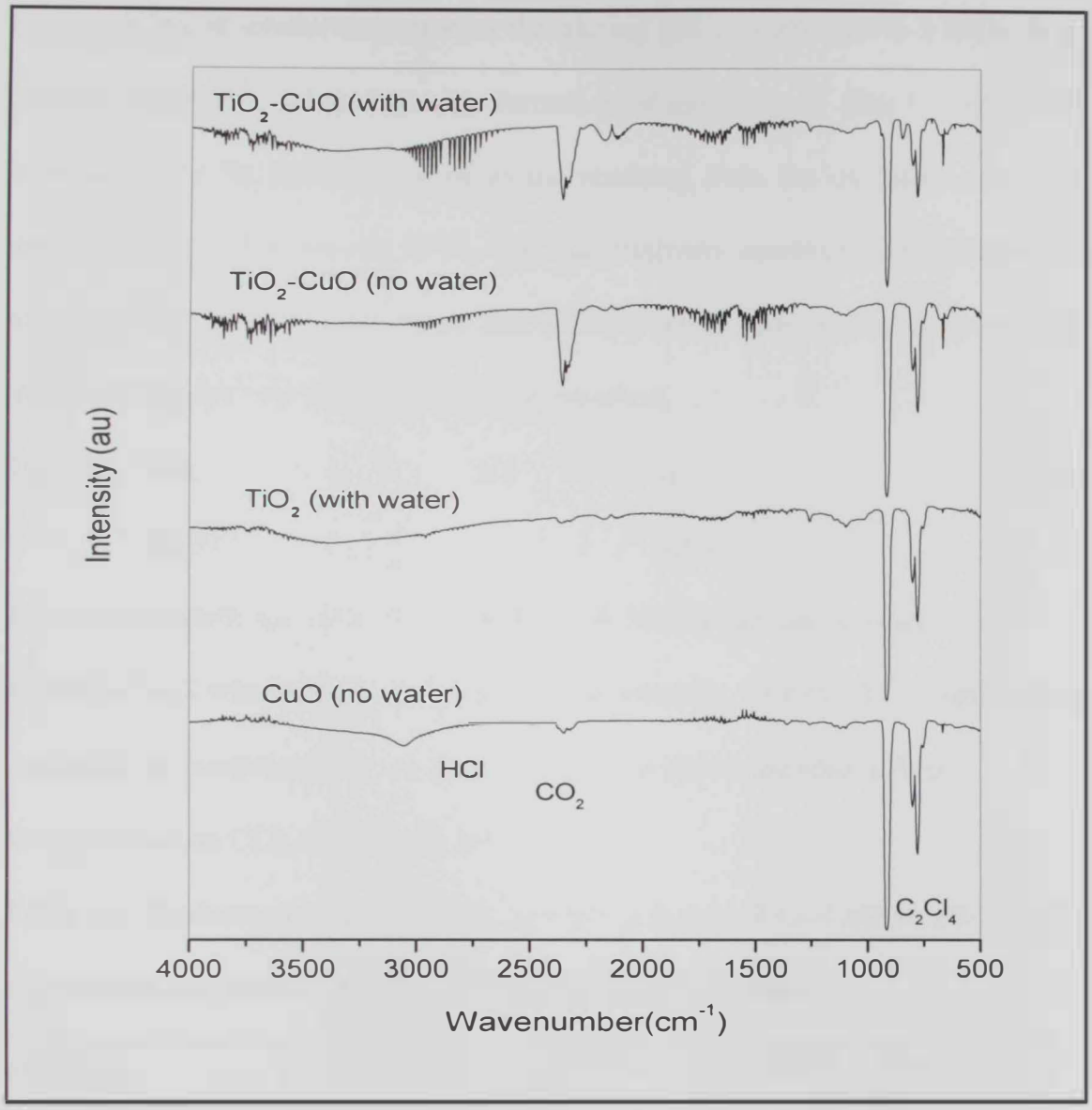

Figure 3.13 FTIR spectra of the gaseous products after the addition of a total of 50 μL C_2Cl_4 over pue CuO, pure TiO_2 and TiO_2-CuO at 400 ºC in the absence and in the presence of water.

In another set of similar experiments the eluting gas was allowed to bubble in an aqueous solution of KI to detect the formation of any Cl_2 gas. The Cl_2 formation is indicated by the brown color of iodine resulting from the oxidation of iodide ions by Cl_2 gas. The amount of Cl_2 was quantitatively determined by titrating the solution with 0.05 *M* sodium thiosulfate solution which reduces the iodine back to iodide turning the brown solution back to colorless,

$$2I^- + Cl_2 \dashrightarrow 2Cl^- + I_2$$

$$I_2 + 2S_2O_3^{2-} \dashrightarrow 2I^- + S_4O_6^{2-}$$

The same solution was also titrated with 0.5 *M* NaOH solution to determine the amount of HCl which dissolves in the aqueous solution. The results obtained from this study are summarized in Table 3.3 which also shows the results from anexperiment on CCl_4 for comparison.

Table 3.3. Products profile from reactions of C_2Cl_4 over TiO_2-CuO at 400 °C with and without the presence of water (1:2 CHC:H_2O molar ratio).

Reagent		Moles of HCl	Moles of Cl_2	% HCl[a]	% Cl_2[a]
C_2Cl_4	With water	8.2×10^{-4}	0	71	0
	Without water	5.0×10^{-4}	0	43	0
CCl_4	With water	7.5×10^{-4}	1.86	60	3

a: These values represent the selectivity to each product measured as the percentage of the original chlorine atoms, in the 30 μL C_2Cl_4 or CCl_4, converted into each product.

From this study it is evident that in the presence of water, more HCl formed as compared with the absence of water. A comparison between the amounts of HCl from the reactions with and without the presence of water can be also inferred from the FTIR spectra (Figures 3.10 and 3.11). The higher selectivity to HCl in the presence of water is interesting since this minimizes the chance for chlorinated products especially the chlorination of the catalyst, which would result in deactivation [10]. No Cl_2 formed in both cases, the presence and the absence of water. It is interesting to compare these results with similar experiments on CCl_4 over TiO_2-CuO in the absence of water where a considerable amount of Cl_2 formed. Besides causing the chlorination of the catalyst, Cl_2 is not a desirable product because it cannot be easily removed from gas streams by simple water scrubbing in contrast to HCl.

Besides the FTIR and the titration studies of the gaseous products, powder XRD analysis was done for the catalyst after reactions in the presence of water. The XRD pattern of the catalyst after reactions was identical to the corresponding one before reaction indicating that the catalyst was regenerated as no significant phase changes occurred. These results again support the potential catalytic activity that

this material possesses for this reaction. Figure 14 shows the patterns of the catalyst before and after the reaction.

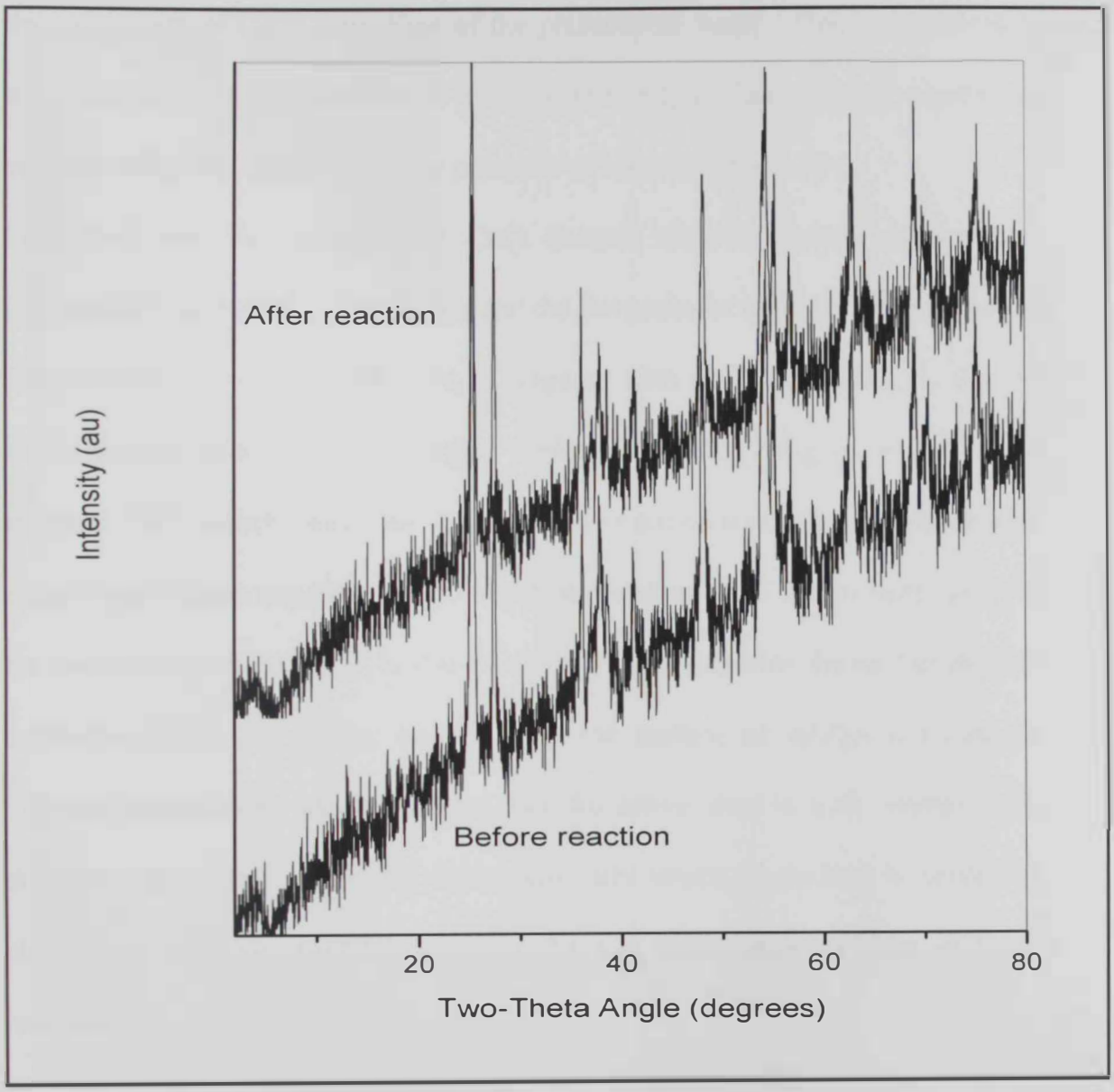

Figure 14. XRD patterns of TiO_2-CuO catalyst before and after reactions with C_2Cl_4 in the presence of water.

3.3.5 Decomposition and Hydrolysis of C_2Cl_4 over Al_2O_3-CuO at 400 °C

Surprisingly, alumina-supported samples showed very low reactivity toward the decomposition of C_2Cl_4 regardless of the presence of water. This is surprising if we compare it with reactions of CCl_4 where Al_2O_3-CuO showed significant catalytic reactivity especially in the presence of water (Figure 3.15).

Compared with TiO_2-CuO, Al_2O_3-CuO showed relatively lower reactivity as indicated by the higher % conversion and the formation of more CO_2 in the case of TiO_2-CuO as shown in Figure 3.16. Compared with pure CuO, less CO_2 formed although Al_2O_3-CuO had much higher surface area (~175 m^2/g vs. ~40 m^2/g for the pure CuO), which means that the reactivity is not only surface-area-dependent. These observations suggest that the transition metal oxide TiO_2 is a better support for the decomposition of C_2Cl_4 than alumina. This study also shows that the two molecules, CCl_4 and C_2Cl_4, interact with the surface of Al_2O_3-CuO through different mechanisms which suggests that the active sites in both reactions are different. It is clear that more work, especially structural studies, is needed to elucidate a possible mechanism and to have a better understanding of these reactions.

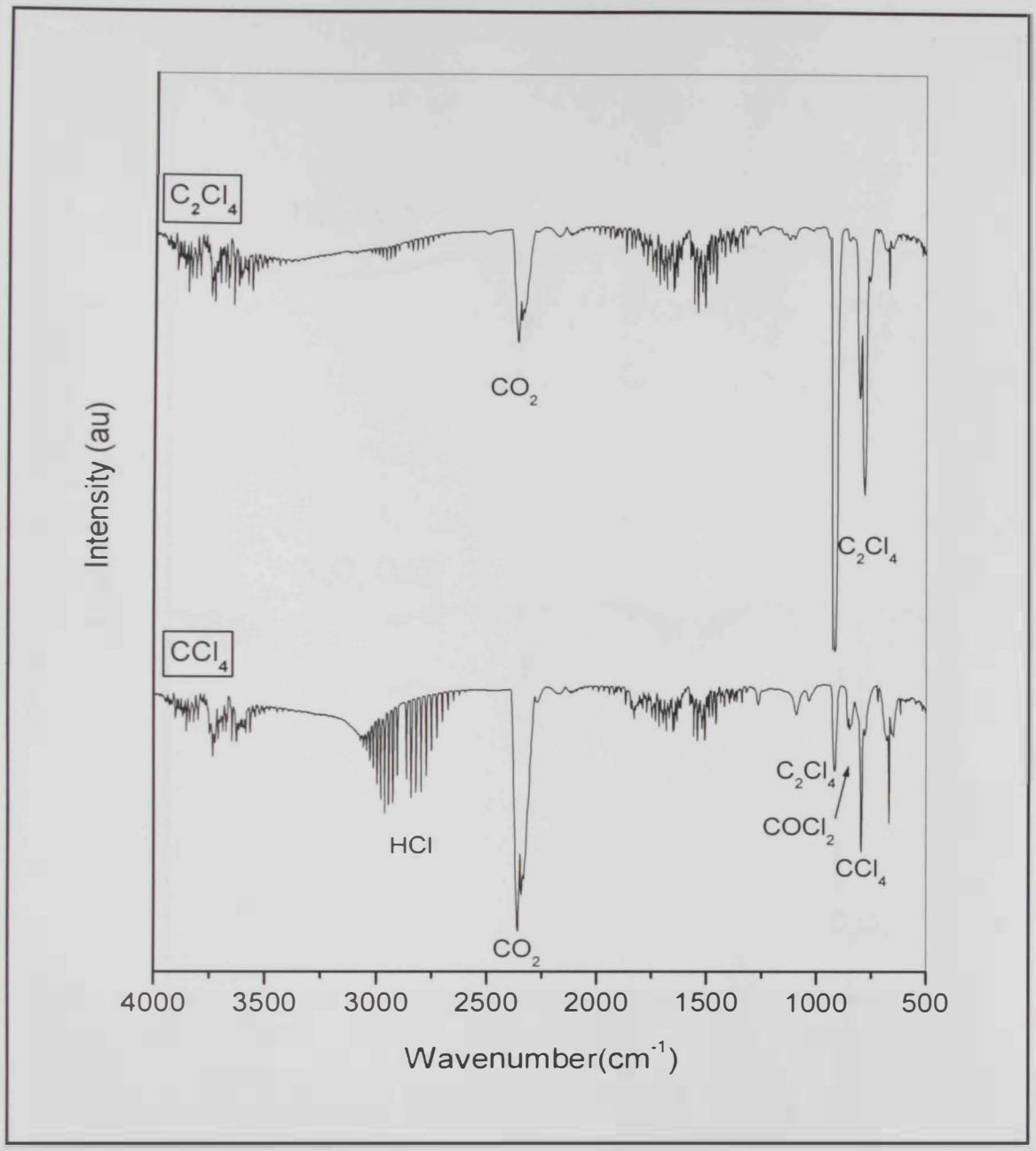

Figure 3.15 FTIR spectrum of the gaseous products from the catalytic hydrolysis of CCl_4 and the corresponding spectrum from the hydrolysis of C_2Cl_4 over Al_2O_3-CuO after the addition of a total of 20 μL reagent.

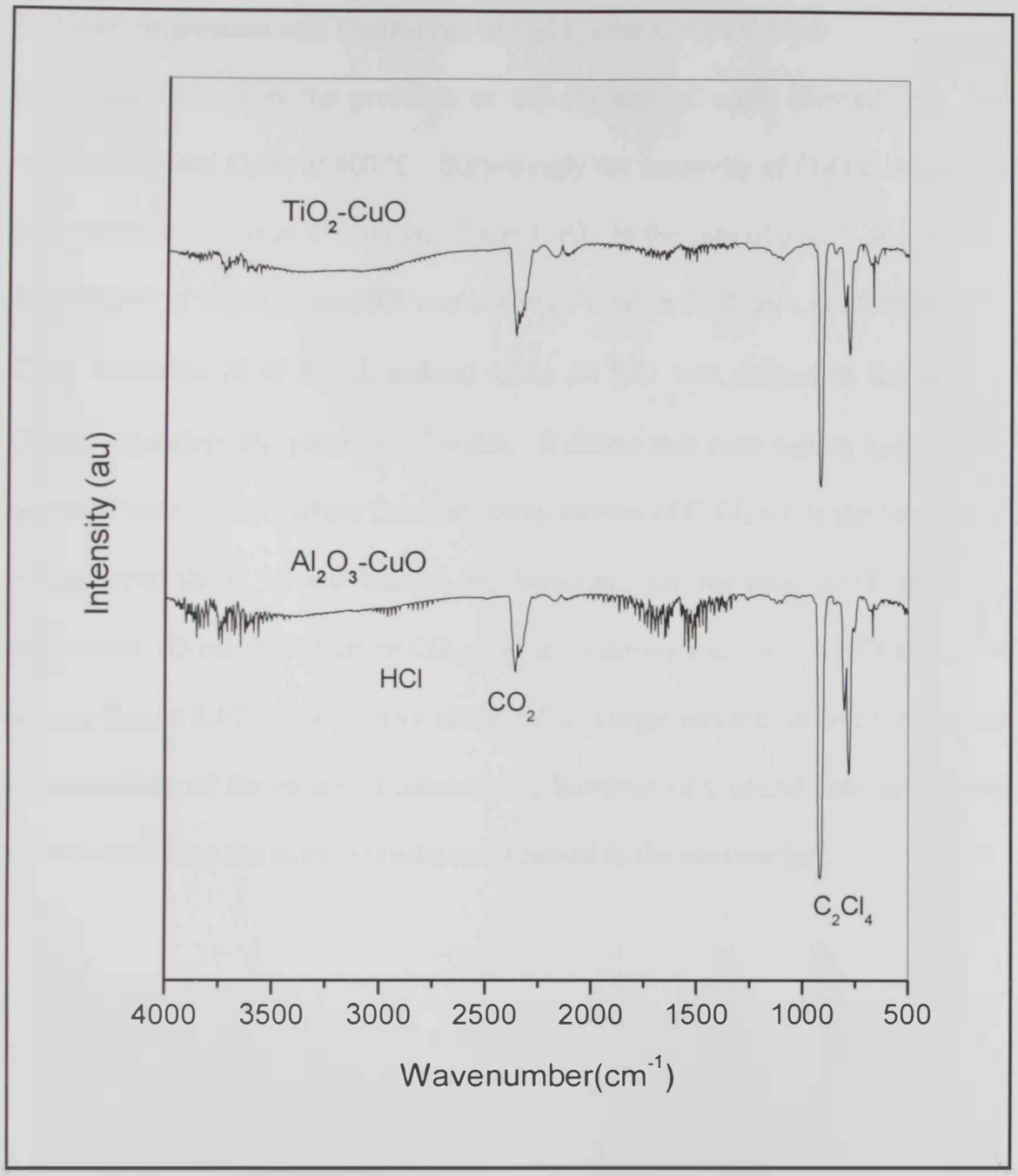

Figure 3.16 FTIR spectrum of the gaseous products from the catalytic hydrolysis of C_2Cl_4 over Al_2O_3-CuO and the corresponding one over TiO_2-CuO after the addition of a total of 20 μL C_2Cl_4.

3.3.6 Decomposition and Hydrolysis of C_2Cl_4 over C and C-CuO

Employing C-CuO in the presence or the absence of water showed very low reactivity toward C_2Cl_4 at 400 °C. Surprisingly the reactivity of CuO/C seemed to be less than that of pure C and that of pure CuO. In the case of pure C and without the addition of water, some HCl was observed (Figure 3.17) as a product from all C_2Cl_4 injections (5 of 10 μL pulses) while no HCl was noticed in the case of CuO/C regardless the presence of water. It seems that pure carbon keeps some adsorbed water on its surface that leads to hydrolysis of C_2Cl_4 while the interaction of CuO with the C surface inhibits this behavior. On the other hand reactions over pure CuO resulted in more CO_2, higher % conversion, and no HCl as can be seen in Figure 3.17. Again, more structural investigations are needed for a better understanding of the nature of interactions, however very useful conclusions can be extracted from the current results as discussed in the next section.

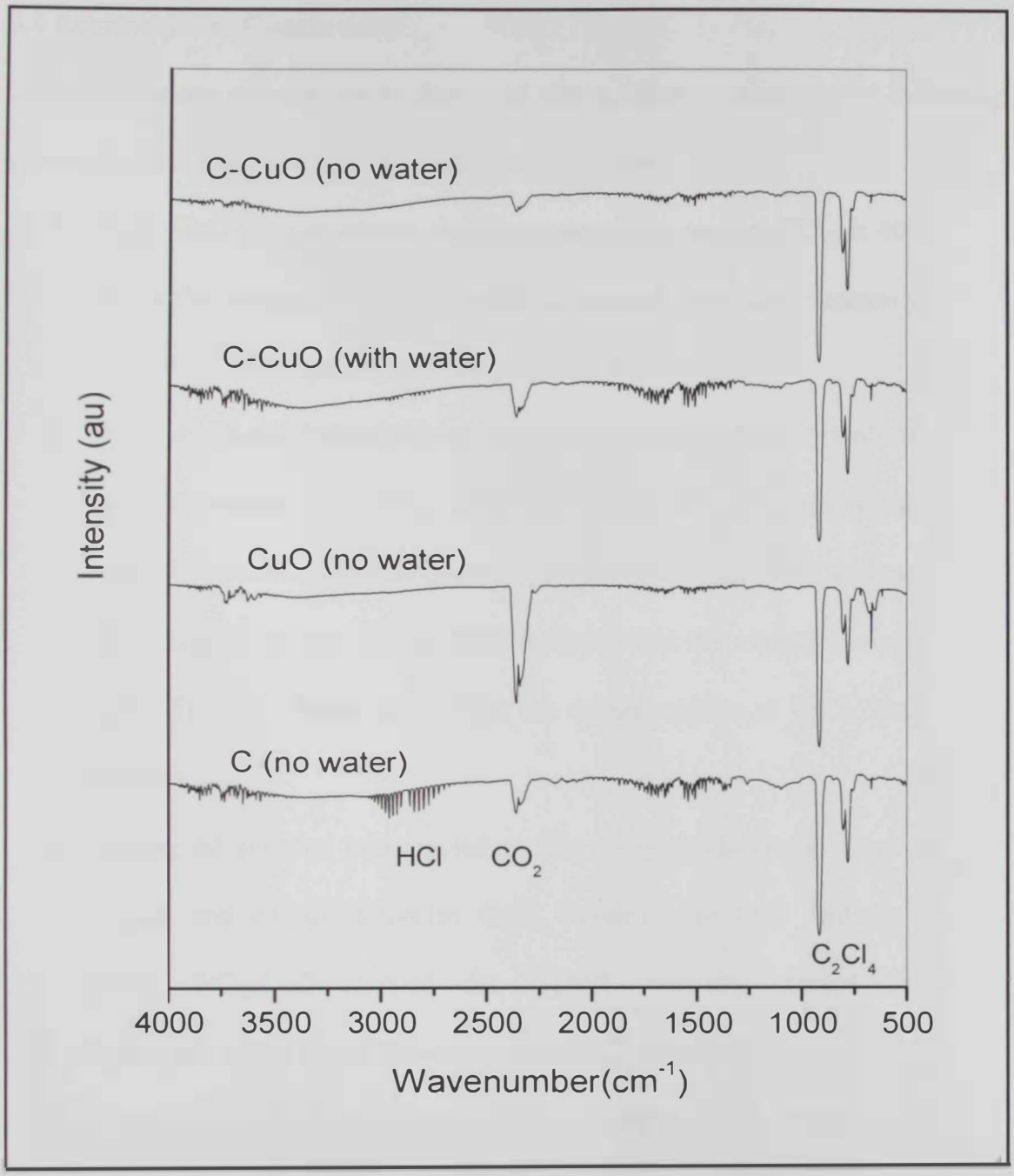

Figure 3.17 FTIR spectra of the gaseous product from the first pulse of C_2Cl_4 over pure C, Pure CuO (B1) and C-CuO in the absence of water at 400 °C.

3.4 Summery and Conclusions

The observations and the results discussed above allow us to make the following general conclusions in relations to the reactivity studies:

1. Al_2O_3-CuO catalyst posses significant reactivity toward CCl_4 at 400 °C in the presence of water while it showed very low reactivity towards the corresponding hydrolysis of C_2Cl_4.
2. While Al_2O_3-CuO showed very low reactivity toward the hydrolysis and conversion of C_2Cl_4, TiO_2-CuO exhibited very promising reactivity toward the same reaction producing CO_2 and HCl without the formation of any $COCl_2$. This indicates that the transition metal oxide TiO_2 is a better support for the decomposition of C_2Cl_4 than alumina.
3. Among all systems investigated in this study (including alumina-, titania- and carbon-supported CuO, besides pure CuO and pure TiO_2), TiO_2-CuO showed the highest reactivity toward the hydrolysis of C_2Cl_4 and its conversion to CO_2 and HCl.
4. The presence of H_2O generally decreased the formation $COCl_2$ and enhanced the conversion to CO_2 and HCl.
5. While some Cl_2 formed from the decomposition of CCl_4 over TiO_2-CuO catalyst, it did not form in the corresponding reactions of C_2Cl_4.

6. CO was not observed in significant amounts as compared with similar processes reported in the literature on different CHC compounds.

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